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# THE CHEMISTRY OF WHEAT FLOUR

BY

C. H. BAILEY

A. C. S. MONOGRAPH NO. 26

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# CHEMICAL ABSTRACTS

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No. 15

## 1—APPARATUS AND PLANT EQUIPMENT

W. L. BADGER

Rectifying column calculations with particular reference to  $n$ -component mixtures. E. V. MURPHREE *Ind. Eng. Chem.* 17, 747-50(1925).—The concept of the theoretical plate does not offer a satisfactory basis of calcn. for rectifying columns when the mixt. being rectified contains more than two components and sometimes two. A method for actual plates with any number of components is developed from the absorption equations. A means of expressing the efficiencies of rectification of the volatile components is given.

Demonstration apparatus for the simultaneous preparation of the halogens. RAYMOND SZYMANOWITZ *J. Chem. Education* 2, 440-1(1925).

Orsat kinks. H. D. FISHER *Power* 61, 799-800(1925). cf. de Graaf, C. A. 19, 1969.—Additional suggestions are made as to the operation of the Orsat app.

A useful modification of the Geissler bulbs. G. ONDO. *Ann. chim. applicata* 14, 3-4(1925).—The vertical tube which in the usual form of app. leads from the first gas bulb down into the first of the 3 KOH bulbs is extended up into the gas bulb and is bent over in the form of a crook so that its open end points downward. This prevents all chances of the KOH soln. spurting back into the CaCl<sub>2</sub> tube when the system is aspirated before using to test the tightness of the joints.

Simple methods for removing frozen-in glass stopcocks and stoppers. E. G. R. ARDAON. *Can. Chem. Met.* 9, 137-9(1925).—Warm with a Bunsen flame the exposed stump of a broken stopper and the lower end of a selected glass stopper (the lower end of which is about the same size as the exposed end of the stump), and attach the 2 firmly by sealing wax. Warm the neck of the bottle in a small flame, press the stopper upward with one hand while tapping upon it from the opposite side at the same time. In cases where alk. solns. have caused sticking, place a piece of rubber tubing (e. g., like that used for Gooch crucibles) over the neck, pour in dil. HCl, insert a funnel or carbon filter tube into the rubber tube, and alternately apply and remove suction until the stopper is loosened. For burets the use of a vise or "C-clamp," with strips of wood to press against the barrel of the stopcock and the end of the stopcock itself, is recommended.

Apparatus for preparing vapor-air mixtures of constant composition. W. P. YANT AND F. E. FREY. *Ind. Eng. Chem.* 17, 692-4(1925).—The liquid to be volatilized is contained in one arm of a modified U-tube, the top of which terminates in a capillary, while the bend is filled with Hg. Water is dropped at a known, const., adjustable rate into the other arm of the tube, causing the Hg to rise in the first arm and to discharge the liquid to be volatilized into an evaporator through which a metered, const. air current is passed. The method and formula used for calibrating the app. are given. Its merits are described.

New apparatus for determining the coefficient of expansion of gases. W. H. CHAPIN AND R. N. MAXSON. *J. Chem. Education* 2, 490-3(1925).—The app. is for instruction of students.

The measurement of the density of porous and pulverulent substances. O. SCARPA. *Ann. chim. applicata* 14, 360-7(1924).—The inconveniences and inaccuracies of the ordinary pycnometer and volumometer methods are overcome by new forms of app. *Pycnometer*. The dried substance is weighed in an ordinary pycnometer and the latter is put in a desiccator with a ground-glass air-tight cover. Through a rubber stopper in the cover runs a funnel, the stem of which is drawn out almost to a capillary. This fine open end leads into the mouth of the pycnometer directly over the substance. Where the stem of the funnel flares into the cup of the funnel is a plug, preferably a rod with a rubber end. The desiccator also has a side-neck so that it can be exhausted by suction. With the pycnometer in position the system is sealed and the desiccator is

exhausted for about 1 hr. The cup of the funnel is then filled with  $H_2O$  free of air and the plug in the funnel is opened so that  $H_2O$  runs in drop by drop and fills the pycnometer, suction being continued. The method is otherwise the same as usual, but is more accurate because of more nearly complete removal of air than long boiling. *Volumenometers*—Two new types are described, which in form and in operation are too complicated for a brief yet adequate description. They are described and illustrated in full detail with the mathematical principles involved, and the original should be consulted. The second is essentially an improved modification of the Oberbeck volumometer (cf. *Lo Surdo Nuovo cimento* 12(1906)). C. C. DAVIS

**Destruction of Berthelot's calorimetric bomb—its replacement by a bomb of new type.** CH. MOTREU. *Compt. rend.* 180, 557-61(1925).—In 1918 this celebrated bomb, after 30 years' service, burst during work on reactions of explosive violence. In replacing it, a great reduction in the amt. of Pt in the lining was necessary. Hence it was necessary to eliminate friction in closing the cover. A Pb gasket was introduced, and the neck was contracted to allow the necessary increased pressure to be used. The new lining was in 3 layers, intimately united, of 0.2 mm. Pt, 0.3 mm. Au, 0.4 mm. Cu. This was strong and insol. and could be soldered to the steel. Also in *La nature* 53, I, 231-3(1925). W. P. WHITE

**Automatic control of low temperatures.** T. S. SLIGHT. *J. Optical Soc. Am.* 10, 691-3(1925). E. H.

**Tools of the chemical engineer. IV. Automatic temperature control.** D. H. KILLEFFER. *Ind. Eng. Chem.* 17, 703-6(1925).—The mechanism and use of several types of automatic temp. control devices and of a humidity controller are discussed and applications pointed out. WM. B. PLUMMER

**Mechanical thermostats.** J. R. ROEBECK. *J. Optical Soc. Am.* 10, 670-90(1925).—A critical review. E. H.

**Design of a thermocouple for measuring surface temperatures.** J. G. KING AND A. BLACKIE. *J. Sci. Instruments* 2, 260-4(1925).—The instrument is used for measuring surface temp. of boilers, etc. and is accurate to 5° in range from 80° to 160°. D. E. S.

**The construction of platinum thermometers.** H. R. LANG. *J. Sci. Instruments* 2, 228-33(1925).—This article describes fully the method of making Pt resistance thermometers as devised by Callendar (*Phil. Mag.* 32, 104(1891); *Trans. Roy. Soc.* 199A, 55(1902)). It describes a useful type of head, also a method of adjusting the fundamental interval to any given value. D. E. S.

**A simple differential air thermometer for use at low temperatures.** W. A. NOYES. *J. Am. Chem. Soc.* 47, 1942-4(1925).—For the approx. detn. of temps. between the b. p. of liquid air and zero. E. J. C.

**A photometer, which is adapted to the grades of sensibility of the eyes as far as possible, and its use as chromatometer, cloud-meter, colloidometer, colorimeter and comparison microscope.** C. FULFACH. *Z. Instrumentenkunde* 45, 35-41, 61-70, 107-10(1925).—The instrument is built especially for the testing of colors in accordance with Ostwald's color-scale. OSCAR PATK

**The microplastometer.** HENRY GREEN AND GEORGE S. HASLAM. *Ind. Eng. Chem.* 17, 726-9(1925).—The app. consists of a thin-walled capillary 0.005-0.02 cm. in diam. mounted for observation under the microscope and connected with a small reservoir (J), an adjustable Hg column for applying pressure to I, and suitable manometers. The capillary is immersed in a mixt. of Nujol and  $\alpha$ -C<sub>10</sub>H<sub>18</sub>Br of the same  $n$  as the glass, and is calibrated vs. liquids of known viscosity by mixing a little ultramarine with the liquid and detg. the velocity of a particle in the center of the stream when the latter is flowing with wall shear only, a ruled and calibrated eyepiece being used. In use as a viscometer the error of the app. is less than 2%. The yield point, or point at which shear commences in the outer liquid layers, is detd. as the point at which particles at varying distance from the axis begin to move with different velocities; the larger particles also beginning to rotate due to the unbalanced forces acting on them; this point may be detd. with about 5% reproducibility. The observed curves for velocity of slippage vs. pressure above this point were not linear and did not intersect the origin. WM. B. PLUMMER

**A microturbidimeter.** O. E. CONKLIN. *J. Optical Soc. Am.* 10, 573-80(1925).—An instrument for measuring the turbidity of emulsions and suspensions, using only a drop of the emulsion, is described. The thickness of emulsion layer necessary to cause the disappearance of an incandescent lamp filament is used as the measure of relative turbidity of the emulsion. Measurements with this app. are reproducible within 2%. Observations on photographic emulsions contg. various concns. of Ag halide showed that the turbidity was proportional to the concn. R. L. DODGE

A micro-furnace for high magnification. H. S. ROBERTS AND TAISIA STADNICHENKO. *J. Optical Soc. Am.* 10, 605-8(1925).—A broad electric heater of nichrome ribbon is so arranged that small amts. of materials between strips of silica glass can be heated and observed through a microscope. The temp. of the charge is measured thermoelectrically. The charge can be maintained in an atm. of inert gas. Details are given. R. L. DODGE

An inexpensive photomicrograph attachment. HENRY LEFFMANN *Am. J. Pharm.* 97, 353-4(1925).—App for direct attachment to the vertical microscope consists of a wooden box about 8 in. high, with interior measurements of  $4\frac{1}{2}$  in. in one direction and  $3\frac{1}{2}$  in. in the other. The lower end is closed by a board about  $\frac{1}{2}$  in. thick, perforated so as to take snugly the draw-tube of the microscope, which is pushed through until the flange abuts on the upper surface of the board. This permits the insertion of an eye-piece if desired. About  $\frac{1}{2}$  in. below the upper rim of the box 2 small rests are fastened. The box should be painted a dead black inside and out, and provided with a well-fitting lid. With slight additional expense the app can be more elaborately constructed. In operation, the ground-glass is laid on the rests, the focus adjusted, the glass removed, a sensitive plate substituted and the lid put on. The box may be modified by making it in the form of the frustrum of a pyramid with the bottom board only about 2 in. sq. In the inexpensive form described the app has proved satisfactory. W. G. GAESSLER

Remarks on the publication of Friedrich Holtz and W. H. F. Kuhlmann: The ultrabalance. W. H. F. KUHLMANN *Ber* 58B, 961(1925); cf. *C. A.* 19, 1356.—Corrections to the previous paper. It is not correct to say that the Pregl microbalance is accurate only to  $\pm 0.005$  mg. R. J. HAVIGHURST

Sprenkel pump. J. J. MANLEY. *Proc. Phys. Soc. London* 37, 142-4(1925).—Further improvements in the design of the pump previously described (*C. A.* 18, 2619). The walls of the pump are freed from gas skins by elec. means and the shattering of the Hg pellets, which tends to liberate gas, is checked by a special construction of the fall tube. G. L. CLARK

High-pressure steam heating. R. TILLMANN *Chem.-Ztg.* 49, 35(1925).—High-pressure steam heating can be used successfully for  $400^\circ$  in the lab. Either gravity flow or pump circulation can be used. Formulas are given for calcg. heat interchange and rate of flow. C. G. KING

Treating with steam in the sieve centrifugal. B. BLOCK. *Chem. App.* 11, 152-4(1924); 12, 45-6, 76, 97-8(1925).—Concluded from *C. A.* 18, 2089. "Treating with a mixt. of steam and air or other gas," and "Comparison of treating crystals in the sieve centrifugal with liquids or with steam" are discussed and some of the advantages of steam treatment pointed out. J. H. MOORE

Universal commutator for potentiometric measurements by the compensation method. A. ERNEST. *Chem. Listy* 18, 250-1(1924). H. G.

Filling mercury manometers. P. F. WEATHERILL. *J. Am. Chem. Soc.* 47, 1947(1925). E. J. C.

Acetylene generator. M. H. COMPTON. U. S. 1,543,058, June 23.

Apparatus for producing carbon-black and steam. W. A. SHARPE. U. S. 1,541,860, June 16.

Apparatus for continuously indicating and controlling the degree of concentration of liquids in evaporating vessels. G. F. WEATON. U. S. 1,543,137, June 23.

Concentrating pan of cast iron high in silicon. O. JACOBSEN, U. S. 1,542,941, June 23.

Thermostat adapted for control of electric heating of liquids. A. S. CURTIS and D. J. BLAYNER. U. S. 1,542,850, June 23.

## 2—GENERAL AND PHYSICAL CHEMISTRY

GEORGE L. CLARK AND BRIAN MEAD

The rise in temperature during the absorption of ammonia and chloroform by wool. LEO BLEYER. *Arch. Hyg.* 94, 347-52(1924).—The total heat produced during the absorption of  $\text{NH}_3$  and  $\text{CHCl}_3$  by wool, detd. experimentally, cannot be explained through heat of condensation alone. The heat of condensation, expressed as percent of total heat, amounts to 40% for  $\text{NH}_3$  and 50% for  $\text{CHCl}_3$ . F. B. SEIBERT

Research and appropriate personnel. A. P. M. FLEMING. *Electrician* 94, 620(1925). C. G. F.

Prof. Dr. W. H. Julius. H. GROOT. *Physica* 5, 113-21 (1925).—An obituary notice with portrait B. J. C. VAN DER HOEVEN

National homage to Dr. Bernardino Antônio Gomes (1762-1823), precursor of the discovery of the alkaloid quinine. A. DE AGUIAR. *Rev. quim. pura aplicada* [3], 1, 133-5 (1924).—A review of the contributions of Gomes on quinine eight years before the announcement of the discovery of this alkaloid by Pelletier and Caventou

M. H. SOULE

Chemical knowledge of the Hindus of old. P. C. RAY. *Quart. J. Indian Chem. Soc.* 1, 225-34 (1925) E. H.

Group examinations in chemistry. F. C. WHITMORE. *J. Chem. Education* 2, 441-2 (1925) E. H.

Some suggested changes in high-school chemistry. G. M. BROWNE. *J. Chem. Education* 2, 447-8 (1925). E. H.

The problem of high-school chemistry. GUY CLINTON. *J. Chem. Education* 2, 471-6 (1925) E. H.

Introduction to the systematic treatment of first-year chemistry. P. M. GLASOR. *J. Chem. Education* 2, 449-56 (1925). E. H.

Suggestions to the teacher of chemistry on poisons and their treatment. R. G. TURNER. *J. Chem. Education* 2, 466-71 (1925). E. H.

An adjustable atomic model. G. O. HIGLEY. *J. Chem. Education* 2, 499-500 (1925) E. H.

The art of lecture-table demonstrating. H. F. DAVISON. *J. Chem. Education* 2, 443-7 (1925). E. H.

Museum reactions. R. A. BAKER. *J. Chem. Education* 2, 480-6 (1925).—Some expts are described which demonstrate reactions that proceed for considerable lengths of time and are, therefore, suitable for setting up in a museum E. H.

A classification of the elements with respect to their properties. H. A. GRAUQUE. *J. Chem. Education* 2, 464-6 (1925).—An arrangement of the periodic table is discussed. E. H.

Some recent representations of the periodicity of the elements. J. G. F. DRUCE. *Chem. News* 130, 322-6 (1925) G. L. CLARK

Second report of the International Commission of the International Union of Pure and Applied Chemistry on the chemical elements. ANON. *J. Chem. Soc.* 127, 913-7 (1925).—Upon the basis of new exptl. work the new table of at. wts. shows small changes for Al, B, Be, Ga, Ge, La, Sb, Se, Si, Sm, Sn and Tl. G. L. CLARK

New determination of the atomic weight of selenium. P. BAUYLANTS, F. LA-FORTUNE AND L. VERBRUGEN. *Bull. soc. chim. Belg* 33, 587-612 (1924).—Se from several com. sources was purified by soln. in dist. concd.  $\text{HNO}_3$ , evapd., the  $\text{SeO}_2$  sublimed 3 times, reduced by  $\text{SO}_2$  to red Se, washed, heated to form red Se, and the process repeated. The 2nd time the reduction is exrtd. out by  $\text{NH}_3$  instead of  $\text{SO}_2$  to avoid contamination with S. The  $\text{H}_2\text{Se}$  was prepd. by decompn. of  $\text{Al}_2\text{Se}_3$  by  $\text{H}_2\text{O}$  or by passing H into molten Se at  $700^\circ$ . The d. of  $\text{H}_2\text{Se}$  was detd. at 1.067 and 0.33 atm. pressure and the compressibility at 1 atm. thus calcd. to be 1.042%. The final weighted and cor. value for d. gave the at. wt. as 79.23. WM. B. PLUMMER

The discovery and properties of hafnium. G. HEVESY. *Chem. Reviews* 2, 1-41 (1925).—An excellent summarizing account. G. L. CLARK

The pyrophoric phenomenon in iron. A. SMITS AND G. WALLACH. *Rec. trav. chim.* 44, 130-1 (1925).—On repeating some earlier expts. on pyrophoric iron (C. A. 8, 2101; *The Theory of Allotropy*, p. 216 (1922); cf. C. A. 16, 1178) some discrepancies seemed to appear. A boat of pure  $\text{FeO}$  was placed in an ignited quartz tube in an elec. furnace. Carefully purified  $\text{H}_2$  was freed from traces of  $\text{O}_2$  by heating over Pt and asbestos and from  $\text{H}_2\text{O}$  by passing through a tower of  $\text{P}_2\text{O}_5$  100 cm. high and then a wash bottle contg. liquid Na + K. When the tube was full of the dry  $\text{H}_2$  the tube was closed and the furnace ignited. The temp. was controlled near the boat with a thermocouple. The boat was cooled in a current of dry  $\text{H}_2$ . Heating for 1 hr. gave Fe as follows: at  $575^\circ$ , clearly pyrophoric;  $600^\circ$ , strongly pyrophoric;  $650^\circ$ , less pyrophoric;  $700^\circ$ , weakly pyrophoric;  $710^\circ$ , very weakly pyrophoric;  $725^\circ$ ,  $750^\circ$  and  $800^\circ$ , non-pyrophoric. The transformation pt. at  $760^\circ$  previously given is not a transformation pt. but the change in that region is due to a powerful continuous alteration in the internal condition. E. J. WITZEMAN

Addition to my work: "The surface energy of crystals and crystal forms." M. YAMADA. *Physik Z.* 25, 52-6 (1925); cf. C. A. 19, 756. G. L. CLARK

The focusing method of crystal powder analysis by X-rays. J. BRENTANO. *Proc. Phys. Soc. London* 37, 184-93 (1925).—Detailed presentation of work abstracted in

C. A. 18, 346. The conditions of reflection of X-rays from a thin layer of crystal powder are such that for any given angle of reflection a surface of double curvature can be found which will reflect X-rays coming from one point, to any other definite point. For an element of this surface, situated so as to be distant from the 2 points by lengths  $a$  and  $b$ , resp., the relation  $\sin \alpha / \sin \beta = a/b$  must be satisfied, where  $\alpha$  and  $\beta$  are glancing angles of incidence and emergence of the X-rays with respect to the surface. An app. for this type of work and a new hot-cathode X-ray tube of simple design are described. The lattice dimensions of NiO are detd. to be  $4.172 \pm 0.004$  Å.

G. L. CLARK

Inorganic crystals. WM. L. BRAGG. *J. Franklin Inst.* 199, 701-2(1925).—A lecture.

G. L. CLARK

The crystal structure of the high-temperature form of cristobalite ( $\text{SiO}_2$ ). R. W. G. WYCKOFF. *Am. J. Sci.* 9, 448-59(1925).—By means of powd. crystal spectra and the theory of space groups the unit cube of high-temp. cristobalite is found to contain 8 mols. of  $\text{SiO}_2$  in the at. positions 8f and 16b (cf. Wyckoff, "The Structure of Crystals"; cf. C. A. 18, 3531),  $a_0 = 7.12 \pm 0.01$  Å at  $290-430^\circ$ ;  $d_{110} = 2.20$ ; closest distance O-Si =  $1.541$  Å. U. The absence of discernible mols. in this form of cryst. silica and the distinctly lower scattering power per electron of O as compared with Si are discussed.

G. L. CLARK

The plastic extension and fracture of aluminium crystals. G. I. TAYLOR AND C. F. ELAM. *Proc. Roy. Soc. (London)* 108A, 28-51(1925).—Extensions and refinements of work reported in *Proc. Roy. Soc. (London)* 102A, 613(1923), for the X-ray analysis. A theory of fracture is presented from which the principal conclusions are (1) with the characteristic stress-strain curve the fracture of Al single crystals cannot occur by slipping on a single plane; (2) the geometrical conditions alone imply that fracture takes place more easily when double slipping occurs than when all the slip is confined to one plane; (3) the specimen should break by double slipping when  $(\epsilon/S)(dS/d\epsilon) = 1$ , where  $S$  is the resistance to slipping per sq. cm. of the slip-plane and  $\epsilon$  is the extension. Unusually valuable information was obtained from the use of stereographic nets.

G. L. CLARK

Strengthening and recrystallization. R. GROSS. *Z. Metallkunde* 16, 344-52 (1924); *Science Abstracts* 28A, 9.—G. attempts to refer deformations of a crystal to a system based on the slip planes  $T$  formed in the crystal, the direction of slip  $t$ , and an axis  $f$ , perpendicular to  $t$ , about which the lattice can be bent. In gypsum there is only 1 definite  $f$  direction, and the conditions are very simple. If a gypsum crystal is split parallel to (010) into thin plates, and bent about the axis [101], cylinders can be obtained with a radius of curvature of less than 1 cm. without any cracks; if the direction is not followed exactly the cylinder consists of a no. of different pieces, each of which is bent round [101], and which meet one another in broken edges. X-rays may be used to confirm this large-scale expt. In metals there are several  $f$  directions, and G. has investigated W wires (single crystals), which were bent in several different directions, and examd. by the Laue method, so as to find the position of the axis  $f$ . Expts. on the bending of rock-salt rods, as depending on load, time of loading, and sectional area of the rod are described, which confirm G.'s previous assumption of a strengthening through the action of slip planes. The effect of the crystal surface on the strength of the rods is investigated, and it was found that the bending strength depends on the inner constitution of the crystal, not on the surfaces. The recovery of crystals after distortion was studied, partly by examn. of etched surfaces and partly by means of Laue diagrams. In rock salt it was found that the distorted substance recrystd. with suitable heat treatment.

H. G.

The extension of Trouton's rule to the fusion of metals. A. JOURNIAUX. *Bull. soc. chim.* 37, 513-8(1925).—Trouton's rule can be applied to the m. p. of metals, providing correct values are taken for the mol. wts. In this case, however,  $K$  varies with temp.:  $\log K = (0.8058/T) - 0.28506 \log T + 1.20096$ . The agreement is very satisfactory for the heavy metals, with the exception of Pt. The alk. metals seem to be diat. in contradiction with previous detns. by different methods, showing them to be monoat.

G. CALINGAERT

Determination of the compressibility of some organic fluids. KARL SCHMIDT. *Ann. Physik* 76, 571-89(1925).—The technic of the piezometer in the detn. of compressibility is given in detail. The relative "apparent" compressibility, defined by the relation  $\gamma = (X - X_0)/(X' - X_0)$ , where  $X$  is the value for the liquid under consideration,  $X'$  for  $\text{H}_2\text{O}$  and  $X_0$  the const. of the piezometer. The following values are recorded in scale divisions per cm. depression of the instrument: PhBr, 0.0023; PhCl, 0.0041;  $\text{CHCl}_3$ , 0.0030;  $\text{PhCH}_3$ , 0.0035;  $\sigma\text{-C}_6\text{H}_4\text{NO}_2\text{CH}_3$ , 0.0049;  $\sigma$ - and  $m\text{-C}_6\text{H}_4\text{NH}_2\text{CH}_3$ , 0.0133

and 0.0151, resp. The result  $0.0032 \approx 0.0033$  is obtained for  $H_2O$ , by taking account of adhesion. Measurements taken at  $18^\circ$  and  $89^\circ$  permit an estn. of the temp. coeff. of compressibility and the heat of compression. H. R. MOORE

Theoretical stoichiometry of the space filling and intermolecular strength, the viscosity, and the ion mobility of liquid organic substances. E. WÖHLASCH. *Biochem. Z.* 153, 120-8(1924), cf. *C. A.* 19, 1515.—From the b. ps, crit. consts., and sp. vol. there are calcd. values for  $\phi$ , the mol. sp. vol.  $J_n$ , the intermol. vol., and  $\psi_n = \phi/V_n$ , the space filling no. for the isomers *n*-hexane and diisopropyl. The vol. of a mol. complex must be greater than the sum of the vols. of the mols. composing the complex. Association apparently increases the mol. sp. vol. giving a corresponding decrease of the intermol. sp. vol.  $\phi$  may be calcd. from the ion mobility  $\mu$ ,  $e$ ,  $g$ ,  $\phi = (123.1/\mu\eta)^2$ . W. D. LANGLEY

The variation in viscosity of a fluid as a function of the volume. JEAN DUBIEF. *Compt. rend.* 180, 1164-6(1925).—The viscosity of a gas is greater than that deduced from the kinetic theory for a perfect gas by the factor  $v/(\sigma - b)$ , where  $v$  is the vol. of the gas and  $b$  is the covol. of van der Waals. This equation is tested satisfactorily on the data of Phillips for  $CO_2$ . EUGENE C. BINGHAM

The viscosity of sirupy condensation products of phenol and formaldehyde. A. A. DAUMOND. *J. Soc. Chem. Ind.* 43, 323-6T(1924).—Changes in viscosity offer a delicate means for control. The viscosity was measured by the Whalley method (cf. Fortsch. and Wilson, *C. A.* 18, 2803), castor oil with 25% glycerol was used as a calibrating fluid. It is found that the log viscosity-temp. graph is linear. Since the curve is linear it is inferred that the soln. is not at first colloidal. The soln. is regarded as contg. *o*-hydroxybenzyl alc., *p*-hydroxybenzyl alc. and dihydroxydiphenylmethane in true soln. EUGENE C. BINGHAM

The velocity function of viscosity of disperse systems. I. WO OSTWALD. *Kolloid-Z.* 36, 99-117(1925).—The deviations of the measurements with a viscometer of many colloid solns. from the requirements of the Hagen-Poiseuille law cannot be attributed to one mech. variable,  $e.g.$ , elasticity, for M. Planck has shown that the deformability of an ideal elastic body depends on 36 parameters and it is probable that the mech. properties of structural colloids are still more complicated. It is suggested that all these deviations be included in the one conception, "structural viscosity." Since the evidence of structural viscosity would be variations of pressure or of the velocity of flow, it can be measured by means of an ordinary or slightly modified capillary viscometer. It would only be necessary to vary the height when filled ( $e.g.$ , lengthen the shank) or to attach a manostat to the viscometer. A very simple pressure viscometer (modification of the O. type) has been devised by means of which the measurement of the velocity function or structural viscosity is as easy as the usual measurements with the capillary viscometer. The equations which have been developed to show the dependence of  $\eta$  or  $\rho$  upon  $p$  with different liquids and exptl. conditions include: (a)  $\eta = k\rho$ ,  $\rho = k\rho t$ , the Hagen-Poiseuille law especially applicable to small tubes, long capillaries and small velocity of flow; (b)  $\eta^2 = k\rho$ ,  $\rho = k\rho^{1/2}t$  developed by Darcy for wide tubes and moderate velocity of flow; (c) 2 equations by Osborne-Reynolds, the first,  $\eta^{1.75} = k\rho$ ,  $\rho = k\rho^{1/1.75}t$ ; for wide tubes and high velocity of flow (for  $H_2O$ ) and the 2nd,  $\eta^x = k\rho$ ,  $\rho = k\rho^{1/x}t$ , where  $x$  varies between 0.5 and 1.0, for almost any exptl. conditions but with very rapid changes in the values for the exponents at certain crit. velocities; (d)  $\eta^{1/n} = k\rho$ ,  $\rho = k\rho^{1/n}t$  for widely different liquids, particularly colloid dispersions with small velocity of flow, and widely varied exptl. conditions and app. O. has also shown that instead of  $\rho t = k$ , the equation  $\rho^{1/n}t = k_2$  or  $t_2 = k_2\rho^{1/n}$ , where  $n$  is 1.0 to 2.0, holds throughout a very wide range. In these equations,  $p$  is the pressure,  $t_1$  and  $t_2$  are the velocities of flow, resp., of the colloid and  $H_2O$  and  $n$  and  $k_2$  are consts. In many cases still better results have been obtained by the equations in the form,  $t_2 = t_1 + k_2\rho^{1/n}$  and  $t_2 = k_2(t_1 - t_1)^{1/n}$ . The corresponding equations for measurements with the Hess app. are, when  $t$  is const.,  $\rho^{1/n}/V_2 = k_1$  and  $(V_2/V_1)\rho^{1/n} = k_1$ ; with the Couette app.  $A_1D^{1/2} = k_1$ .  $V_2$  and  $V_1$  are the vols. resp. of the colloid and the  $H_2O$ ,  $A_1$  is the deflection in degrees through the colloid and  $D$  the reciprocal of the velocity of rotation. The validity of these relations for measurements with a capillary viscometer is shown in 20 tables for about 25 different solns. Measurements were made with 7 different app. by about 8 different experimenters. The sols. measured included:  $V_2O_5$ , benzopurpurin, cotton yellow, Na stearate, Hg sulfosalicylate, agar, tragacanth, gum arabic, gelatin of different concns. and heat treatment, viscose, India rubber in toluene, xylene and benzene. The av. difference between the measurements and the calcd. values seldom exceeded 2% and with the more carefully measured values was less than 1%. II. *Ibid*

157-67.—The general equations previously developed for the velocity function of structural colloids have been shown to be valid not only for the capillary viscometer but also for measurements with the Hess app. and with the Couette app. When compared with measurements made by Hess, Rothlin, Freundlich and Schalek with the Hess app. for sols of  $V_2O_5$ , benzopurpurin, gelatin, egg white, agar, starch and soap, the velocity function could be calcd. within 1 to 2% error. When the pressures were less than 1 cm. of Hg, the error was very large. When compared with measurements made by Hatschek, Freundlich and Schalek with the Couette app. for cotton yellow and gelatin, the error was 1.7 to 2.4%. The values for  $n$  as detd. for all the different conditions were between 1 and 2. IV. *Ibid* 248-9.—The simple logarithmic relation between viscosity and the velocity of deformation has been used for the special cases of vaseline and starch paste by de Waale (cf. C. A. 18, 3501) and by Farrow and Lowe (cf. C. A. 18, 606). O. has drawn the following conclusions from the work described in this series of articles: (1) This logarithmic function is valid for about 25 different kinds of sols in capillary viscometers of very different kinds. (2) The same relation holds for measurements with the Hess and the Couette app. and consequently has a very general application. (3) The relation of this function to the Hagen-Poiseuille Law and to the symmetrically adjoining field of anomalous viscosity (at higher pressures) has been developed and thereby the importance of the logarithmic equation extended. The behavior in both fields of anomalous viscosity may be represented by the same logarithmic equation with this algebraic distinction, that with the higher pressures the exponent of the pressure is made  $< 1$  and with the lower pressures  $> 1$ . H. M. McL.

Some physical-chemical properties of mixtures of ethyl and isopropyl alcohols. GEO. S. PARKS AND K. K. KELLEY. *J. Phys. Chem.* 29, 727-32 (1925), cf. C. A. 18, 2832.—EtOH and Me<sub>2</sub>CHOH of various mol. ratios conform within exptl. error to the ideal laws of mixts., since (1) a very small evolution of less than 13 cal. per mol. takes place on formation of the several solns., (2) the vol. shrinkage is less than 0.01%, (3) observed vapor pressures of the resulting liquid are in close agreement with those calcd. from Raoult's law, (4) refractive indices are straight line functions of the wt. compons., and lastly (5) the observed viscosities give only a negative deviation of less than 0.4% from Kendall's equation  $\eta^{1/2} = X_1\eta^{1/2} + X_2\eta^{1/2}$ . H. R. MOORE

The calculation of the  $p$ - $x$  curves of binary liquid mixtures. L. FRANK. *Ber.* 58B, 982-4 (1925); cf. following abstr.—By means of the partial pressure formula and Duhem's equation, a formula was derived, from which partial and total pressures and compn. of the vapor phase could be calcd. with fair accuracy for a no. of binary systems.

A. W. FRANCIS

\* Property-composition curves of binary liquid mixtures. L. FRANK. *Z. physik. Chem.* 114, 257-74 (1924).—The possibility of interpreting property-compn. curves in terms of the van der Waals equation is considered. The properties include vapor pressure, b. p., sp. vol., viscosity, surface tension, and partial pressure, and 43 binary mixts. have been examd. It has been found that the assumption of compd. formation or association can be frequently dispensed with, although in some cases, e. g.,  $\text{CHCl}_3$ -EtO,  $\text{CS}_2$ -acetone, mixts. of benzene with MeOH, EtOH, AcOH and  $\text{CS}_2$ , and nearly all mixts. with water, satisfactory results are not obtained. The mixts. with water are regarded as ternary mixts., perhaps with  $(\text{H}_2\text{O})_n$  and  $(\text{H}_2\text{O})_m$ , while almost all other mixts. for which calcd. and exptl. values do not agree contain an associated component. On the other hand, the b. p.-concn. curves show fairly good agreement between calcd. and observed values with EtO-MeOH and EtO-EtOH, although the alcs. are associated, and the viscosity values also seem to be largely unaffected by association. The vapor pressure-concn. curves for MeOH-EtOH give good agreement, a fact for which the explanation suggested is that over the temp. range considered (20-100°), both components are associated to the same extent.

B. C. A.

Soap films as detectors: stream lines and sound. JAMES DEWAR. *Proc. Roy. Inst. Gr. Britain* 24, 197-259 (1925).—The films were made with 10 parts of glycerol to one part of oleate soap made from pure oleic acid and ammonia, triethylamine, tetraethyl- or tetramethylammonium. Varying amts. of water were used. After the film was formed air jets were allowed to impinge and the whole was illuminated and projected on to a screen or photographed. Beautiful color changes are noted and many patterns are reproduced. This serves as a method for the graphical study of sound waves. The effect of the velocity of the jet was studied and some results on the magnetic properties of air, O, He, H and NO are given. The piercing of films by liquid or solid shot was observed and a method of forming multiple films was worked out. F. O. A.

The behavior of olive oil and of oleic acid toward water. J. F. CARRIÈRE. *Rec. trav. chim.* 44, 121-9 (1925).—From the material given in this paper and the preceding

paper (C. A. 18, 2628) the following conclusions were drawn. The complicated manner in which a drop of oil behaves on water cannot be explained by a hydrolysis of the oil, as is often stated, but should be attributed to fatty acids and other impurities in the oil. Absolutely neutral oil behaves differently on water. The interfacial equilibria absolutely neutral oil—H<sub>2</sub>O and oleic acid—water establish themselves immediately; this is not true of the equilibria between a mixt. of oil and fatty acids with water. Traces of fatty acids in the oil are revealed by the influence of NH<sub>4</sub>OH vapor on the surface phenomena by giving rise to movements. The values for the interfacial tension for neutral oil—water and oleic acid—water are about 26 and 10.5 dynes/cm, resp., at 20°. C. proposes to call that part of a surface or of a monomol interfacial layer which is occupied by a single mol. group, aligned according to the theories of Langmuir and Harkins, the "mol. field." In the monomol. surfaces or layers which are satd. with polar substances the value of the tension is directly proportional to the magnitude of the mol. field. There is a simple mathematical relation between the values of the surface tensions of water satd. with triolein or oleic acids and their interfacial tensions. In applying the above principles C. calculates the values of the mol. fields in the satd. surfaces and the interfacial layers of triolein-water and oleic acid-water. E. J. WITZEMANN

Surface layers on glass. R. SISSINGH. *Physica* 5, 77-83 (1925), cf. *Arch. Neerl.* ser. III, 8A, 142 (1924).—Light rays reflected by an old glass prism showed considerable elliptical polarization due to a surface layer of appreciable thickness ( $d$ ). By a modification of the older theories of Cauchy and of van Ryn van Alkemade it is possible to calculate  $d$ . In the sample mentioned  $3.0 \times 10^{-4}$  mm. was found, after grinding  $1.0 \times 10^{-4}$  mm. The first layer probably consisted of water, the last of air. B. J. C. VAN DER HORVEN

Adsorption of catalytically poisonous metals by platinum. I. Adsorption of lead and mercury. E. B. MAXYEO. *J. Chem. Soc.* 127, 73-7 (1925).—The adsorption of Pb and Hg ions are linear functions of their respective bulk concns. up to the point of satn. of the Pt, when it becomes const. The poisoning curve, i. e., that showing the decrease in catalytic activity, has also been shown to be a linear function of the concn. of poison over the greater portion of the curve. Thus the activity of the catalyst in the presence of such a poison is, at any rate for the first stage, a linear function of the actual concn. of poison on the surface of the catalyst. The question whether the break in the poisoning curve occurs at incipient satn. of the catalyst with the poison is being investigated. A. E. S

Sorption of nitrous oxide and sulfur dioxide by glass. D. H. BANGHAM AND F. P. BURR. *J. Phys. Chem.* 29, 540-50 (1925); cf. C. A. 18, 1933, 19, 1215.—The adsorption of N<sub>2</sub>O by glass is similar to that of CO<sub>2</sub>. For any series of expts. at const. pressure log adsorption is a single-valued function of log ( $p^{\frac{1}{2}}/p_0$ ), the relationship approximating more closely to the linear than with CO<sub>2</sub>. The behavior of SO<sub>2</sub> is similar but it was not possible to find the pressure exponent because of the difficulty in removing all gas from the adsorbent. HARRY B. WEISER

Adsorption of vapors by silica gel by a dynamic method. W. A. PATRICK AND L. H. ORDYCKE. *J. Phys. Chem.* 29, 601-9 (1925).—The adsorption of C<sub>2</sub>H<sub>5</sub>OII, CCl<sub>4</sub>, C<sub>6</sub>H<sub>6</sub>, and H<sub>2</sub>O were measured by a dynamic method in the presence of air. The adsorption of all liquids except H<sub>2</sub>O was in complete accord with the capillary theory of adsorption expressed by the equation  $V = K(p\delta/p_0)(1/m)$  where  $V$  is vol. of vapor adsorbed per g. of gel,  $p$  is the partial pressure at equil. of the vapor adsorbed,  $p_0$  is the satn. pressure at the temp. in question,  $\delta$  the surface tension;  $K$  and  $m$  are consts. No hysteresis was observed except in the case of H<sub>2</sub>O. The anomalous behavior of H<sub>2</sub>O as regards hysteresis, time required for equil. and disagreement with the capillary theory has been accounted for by the increase in viscosity of the adsorbed H<sub>2</sub>O due to decrease in internal pressure brought about by capillary and surface-tension forces. HARRY B. WEISER

Emulsions. I. Types of hydrocarbon-oil emulsions. WM. SEIFRIZ. *J. Phys. Chem.* 29, 587-95 (1925).—Petroleum distillates emulsified with H<sub>2</sub>O and casein form emulsions as follows: fine, stable oil-in-H<sub>2</sub>O type if the sp. gr. is less than 0.820; coarse, unstable oil-in-H<sub>2</sub>O when sp. gr. is 0.820-0.828, no emulsion when sp. gr. is 0.828-0.857; moderately stable H<sub>2</sub>O-in-oil when sp. gr. is 0.857-0.869, and fine, stable H<sub>2</sub>O-in-oil when sp. gr. is above 0.869. There appears to be no relation between surface tension value of oil and type of emulsion as demanded by Bancroft's theory of emulsification (C. A. 7, 2881). The oriented mol. wedge hypothesis of Langmuir (C. A. 10, 3008), (Finkle, Draper and Hildebrand (C. A. 18, 607), and Harkins and Keith, (C. A. 18, 2095) appears inadequate in its present form. The hypothesis demands a monomol. film or a membrane of the order of mol. dimensions; while the membranes actually observed were

optically visible. II. Effect of electrolytes on petroleum-oil emulsions. *Ibid* 595-600.—The behavior toward electrolytes of certain petroleum-oil emulsions stabilized by casein, bears no apparent relation to the valency of the ions nor to the surface-tension changes between the oil and the aq. casein occasioned by the electrolytes. H. B. W.

The behavior of permanently deformed gels on drying. EMIL HATSCHEK. *Kolloid-Z.* 36, 202-6(1925); cf. C. A. 16, 1887, 19, 202.—Fifteen g. of a special hard French gelatin was mixed with 100 g. of H<sub>2</sub>O and satd. with thymol. Square prisms 32 mm X 32 mm X 110-130 mm were cast in paraffined paper forms and allowed to stand at least 24 hrs. The prisms were then permanently deformed by bending or by twisting. During deformation the prisms were covered by vaseline to prevent evapn. or infection. Later the vaseline was washed off with benzine. When a bent prism dried, the ends became clubbed and the amt. of bending increased. Some of the prisms were put in clamps at each end and twisted. When the deformation was permanent they were dried. When the torsions before drying were 28°, 31° and 62°, the torsions after drying were 159°, 168° and 433°, resp. When prisms were cast in a curved shape or cast twisted and later dried no increase of curvature or twist appeared as drying progressed. Then, the increased deformation was due to the stress applied after the gelatin was set, and not to the shape of the object. Diffusion expts. show that stress sufficient to press a prism into the form of a circle does not cause such an internal rearrangement of the gelatin that diffusion rates in different directions are unequal. F. E. BROWN

Stability of colloidal solutions. III. Influence of negative ions, the effect of dilution, and aging, and the influence of capillary active nonelectrolytes on the coagulation of copper ferrocyanide sol. K. C. SEN. *J. Phys. Chem.* 29, 517-39(1925); cf. C. A. 19, 1517.—An extension of previous studies using Cu<sub>2</sub>Fe(CN)<sub>6</sub> sol. and a reaffirmation of conclusions previously given. HARRY B. WEISER

Theory of peptization and protective effect of colloids and nonelectrolytes. K. C. SEN. *Kolloid-Z.* 36, 193-202(1925), cf. C. A. 18, 2449.—When hydroxides are peptized by acids, H-ions are adsorbed. When the negative ions are multivalent they are often adsorbed in quantities sufficient to ppt. the colloid. In the peptization of hydroxides by metallic salts in soln. the active agent is the H ion. A definite chem. action accompanies the adsorption. Only ions and charged colloids may act as peptizing agents. Non-electrolytes and proteins do not truly peptize, though they may indirectly affect the stability of colloids by encasing an already formed particle. This stabilizing is effective only in the presence of electrolytes. Protective colloids may be effective by changing the Hofmeister series of ion adsorption. Protected colloids owe their stability to the Helmholtz double layer. Glycerol, sugar, destin and crystd. egg albumin protect in the same way though they are very different substances. It is difficult to ascribe the protective action of gelatin to its soly. instead of to the Helmholtz double layer as Loeb has done. This would put gelatin in a group apart from the other protective substances. The non electrolytes differ from the proteins in that the covering layer of a protein is more difficult to break down. The previously published theory of Liesegang-ring formation was confirmed (cf. C. A. 18, 2630) by the behavior of Ag<sub>2</sub>CrO<sub>4</sub> gel. When AgNO<sub>3</sub> is added the yellow gel becomes red because of coagulation. F. E. BROWN

A quantitative study of the protection produced in a colloidal solution by the addition of an electrolyte in an amount too small to cause flocculation. A. BOUTARIC AND (MLLE.) G. PERREAU. *Compt. rend.* 180, 1337-40(1925), cf. C. A. 18, 3511 and following abstr.—Increasing vols. of 0.1 N H<sub>2</sub>SO<sub>4</sub> were added to (A) 0.435 g. of gamboge in 25 cc. of water and to (B) the same suspension which had previously been treated with 2.5 cc. of 0.01 N H<sub>2</sub>SO<sub>4</sub>. The min. quantity of H<sub>2</sub>SO<sub>4</sub> which would produce flocculation was more than twice as large for B as for A. The min. for B,  $\beta$ , decreased by the min. for A,  $\alpha$  (or  $\beta - \alpha$ ) is a measure of the protection produced by the small first addn. Varying small quantities of LiCl were added to As<sub>2</sub>S<sub>3</sub> sol. and 11 hrs. later pptn. was effected by the addn. of the min. required amts. of LiCl. When  $\beta - \alpha$  was plotted against cc. of 0.306 N LiCl first added to 100 cc. of sol. a sharp max. appeared at about 3.5. The value of  $\beta - \alpha$  at the max. was about 6 cc. When the preliminary addn. was less than 1.5 cc. or more than 5 cc., the value of  $\beta - \alpha$  was small. The optimum quantity of LiCl was added to several samples of As<sub>2</sub>S<sub>3</sub> sol. and the min. amt. of LiCl required to flocculate was detd. after the lapse of different periods of time. The value for  $\beta - \alpha$  rises rapidly for 8 hrs., remains nearly const. for 16 hrs., falls to about 1/2 of its max. value in 8 hrs. and then remains nearly const. up to about 48 hrs., where the curve ends. In the case of gamboge the larger the preliminary addn. of H<sub>2</sub>SO<sub>4</sub>, the greater the value of  $\beta - \alpha$ . Also in *Rev. gen. colloides* 3, 12-36(1925). F. E. BROWN

The flocculation of colloidal solutions. A. BOUTARIC. *Bull. sci. acad. roy. Belg.*

10, 560-70(1924); cf. preceding abstr.—The flocculation of colloidal sols. has been followed by detg. the rate of change of the opacity by means of a Fery spectrophotometer. In general the opacity increases rapidly after the addn. of the coagulant but slows down as the time of actual pptn. approaches. With 50 cc. of an  $As_2S_3$  sol (3.1 g./l.) and 50 cc. of  $AlCl_3$  sols. contg., resp., 9, 8 and 7 cc. of 0.001 N  $AlCl_3$ , the times required to reach the same opacity (i. e., the same degree of coagulation) were, resp., approx. 1, 7 and 130 min. Similarly for a gum mastic sol (0.668 g./l.) with an equal vol. of acid contg., resp., 19, 17 and 15 cc. of 0.01 N  $H_2SO_4$ , the times for equal coagulation were, resp., 3, 8 and 20 min. Shaking in general increased the rate of coagulation and especially hastened the time at which actual pptn. took place. WM. B. PLUMMER

The influence of light on the coagulation of colloidal solutions. A. BOUTARIC AND Y. MANIÈRE. *Bull. sci. acad. roy. Belg.* 10, 571-7(1924).—The rate of flocculation was detd. as in the preceding abstract. For sols of gum mastic, gum guttae, and  $Fe(OH)_3$ , no difference was perceptible for the 3 cases of darkness, red light and blue light. For  $As_2S_3$  sols the red rays had no effect; the blue rays apparently caused a slight acceleration when  $AlCl_3$  or  $KCl$  was the coagulant, but a slight retardation when  $BaCl_2$  was used. In general light has no effect on the phenomenon. WM. B. PLUMMER

Cataphoresis of metal sols in organic dispersion mediums. F. EYERS. *Kolloid-Z.* 36, 206-7(1925); cf. C. A. 19, 1647.—Harries and Evers observed Pt-rubber colloids which contained particles of positive nature and simultaneously particles of negative nature before those observed by Hatschek and Thorne. Acetone and alc. coagulate the colloid. The Pt remained with the rubber in coagulation or elec. deposit. The pptd. Pt was easily peptized. F. E. BROWN

The solubility of calcium fluoride in acetic acid. L. DUFAR, P. WENGER AND G. GRAZ. *Helvetica Chim. Acta* 8, 280-4(1925).—The soly. of  $CaF_2$  in mineral acids has been detd. by boiling 0.5 g. in 25 cc. of acid for 15 min. for 2 N, N and 0.5 N  $HCl$  and  $HNO_3$ . The %'s of the (0.5 g.) total which was dissolved were, resp., 51.0, 33.0, 21.9; 48.7, 30.3, 20.3. For  $AcOH$  the detns. were made with 300 cc. of acid and 1 g.  $CaF_2$  shaken in a thermostat at various temps. The results are shown as straight-line functions of temp. or acid concn. The solubilities (g./100 cc.) are as follows for 2 N, N and 0.5 N  $AcOH$ , resp.: at 40°, 0.0192, 0.0175, 0.0153; at 100°, 0.3000, 0.0261, 0.0229. WM. B. PLUMMER

Volumetric method of measurement of the mutual solubility of liquids. Mutual solubility of the systems ethyl ether-water and isoamyl alcohol-water. I. A. KABLUKOV AND V. T. MALISCHIEVA. *J. Am. Chem. Soc.* 47, 1553-61(1925), cf. C. A. 17, 2210.—Detns. were made from 10° to 30° for the first system and from 15° to 30° for the second. The method is discussed. B. H. CARROLL

Equilibrium between liquid and gaseous phases of aqueous solutions of hydrogen chloride and of hydrogen bromide. M. S. VREVSII. *Z. physik. Chem.* 112, 109-10(1924).—Theoretical. The change of vapor pressure of binary sols. with temp. and heat of formation is examd., and an expression derived with which the data available for  $HCl$ ,  $HBr$  and  $HI$  sols. are shown to be in agreement (cf. C. A. 18, 1421). B. C. A.

Equilibrium between vapor and liquid of aqueous solutions of ammonia. M. S. VREVSII. *Z. physik. Chem.* 112, 117-27(1924).—Theoretical. Data now available (cf. C. A. 18, 1421) are shown to be in agreement with values calcd. from thermodynamic considerations. B. C. A.

Velocity of hydrogen ions in gels. R. I. LIESEGANG. *Z. Elektrochem.* 30, 449(1924); *Science Abstracts* 28A, 79.—An explanation of the observation of the inertia of the  $H$  ion by change of voltage based upon diffusion. (Cf. C. A. 18, 973.) H. G.

Velocity of hydrogen ions in gels during electrical conduction. N. ISGARISHEV AND A. POMERANIEVA. *Z. Elektrochem.* 31, 101(1925); cf. C. A. 18, 929.—Reply to Liesegang (preceding abstract). E. R. SCHIERZ

Study of the electrolytic transportation. Mobilization of ions by intermolecular exchange. W. MESTREZAT AND Y. GARREAU. *Compt. rend.* 180, 1266-8(1925).—From the theories of Ostwald on the electrolytic double layer and of Arrhenius on the ionic chains, it is shown theoretically how two ionogens sep'd. by a membrane impermeable to the one of their ions may exchange the other ion if both are of the same sign. In the same manner a second ionogen added to an electrolyte may induce the faster ions to circulate without changing the rate of diffusion of the slower ones. JOHN T. SYEAT

Notes on a new method for determining hydrogen-ion concentration. GEORGES HUGONIN. *Curr. tech.* 14, 210-7(1925).—The spectroscopic method is discussed. H. B. MERRILL

The strength of halogen acids. J. ENCKE. *Naturwissenschaften* 13, 393-4 (1925).—For groups of alkyl halides, notably MeI, EtI and PrI, the ratio  $\lambda = p/c$  ( $p$  is vapor pressure of pure ester in mm Hg,  $c$  is concn of the satd. soln of ester in water in millimol per l.) increases with the length of the chain and is proportional to the mol vol  $V$  of the ester. For PrCl at 25°  $\lambda = 11$  and with a value  $V(\text{PrCl}) = 3V(\text{C}_2\text{H}_5)$   $\lambda_{\text{PrCl}}^{25} = 4.6$ , if the acid is taken as the lowest member of the ester series. From Linhart's value  $p_{\text{HCl}}^{25} = 27 \times 10^{-3}$  mm,  $\text{HCl}$  at 25° becomes  $0.59 \times 10^{-3}$  mole per l and the equl const  $K = c(\text{HCl})^2/c(\text{H}_2\text{O})$  of the order  $10^7$ . This value corresponds satisfactorily with the value  $10^6$  of Schreiner (*C. A.* 19, 1050), if the possibility of anomalous behavior of the strongly polar HCl is considered. B. J. C. VANDER HOEVEN.

The nature of the non-dissociated acids. A. HANTZSCH. *Z. Elektrochem.* 31, 167-72 (1925); cf. *C. A.* 19, 1295. Polemical. E. R. SCHIERZ.

The so-called poisoning of oxidizing catalysts. CHARLES MOUREU AND CHARLES DUFRASSE. *J. Chem. Soc.* 127, 1-11 (1925). Certain combustible gases prevent combustion of  $\text{H}_2$  in presence of finely divided Pt and it is said that the catalyst is poisoned. The same gases, however, also prevent  $\text{H}_2$  from burning in  $\text{O}_2$  under the influence of the elec. spark. Since one cannot reasonably speak of poisoning an electric spark, the term poisoning is rejected by the authors as misleading, and also the interpretation, which supposes the formation on the catalyst surface of a layer which tends to insulate it from the gaseous mixt. Poisons for catalysts of autooxidation are invariably oxidizable substances and their effect is termed antioxygenic. They act by catalytically decomposing the peroxide which results from the union of the autooxidizable substance with a mol of oxygen. If this latter is an ordinary catalyst one obtains poisoning. In the case of Pt the reactions may be represented as  $\text{Pt} + \text{O}_2 = \text{Pt}(\text{O}_2)$ ;  $\text{Pt}(\text{O}_2) + \text{B} = \text{Pt}(\text{O}) + \text{B}(\text{O})$ ;  $\text{Pt}(\text{O}) + \text{B}(\text{O}) = \text{Pt} + \text{B} + \text{O}_2$ . Here B is the antioxygen. This explains not only the poisoning of a catalyst but also the results with the elec. spark where H plays the part of the Pt in the above scheme and the interfering gases are the antioxygens. A. E. S.

The heterogeneous water vapor and carbon dioxide dissociation equilibria over iron and its oxides. I. KONRAD HOFMANN. *Z. Elektrochem.* 31, 172-6 (1925).—From data contained in the literature H. derives equations for the heterogeneous equil. of the system  $\text{Fe-O-C}$  over  $\text{Fe}_3\text{O}_4/\text{FeO}$ .  $\log K_{p,g} = (-1615/T) + 1.935$ ;  $\text{FeO/Fe}$ .  $\log K_{p,g} = + (813/T) - 1.140$ ;  $\text{Fe}_3\text{O}_4/\text{Fe}$ .  $\log K_{p,g} = + (251/T) - 0.325$ . For the system  $\text{Fe-O-H}$  over the same solid phases the equations are  $\log K_{p,w} = - (3237/T) + 3.509$ ;  $\log K_{p,w} = - (834/T) + 0.626$ ;  $\log K_{p,w} = - (1452/T) + 1.411$ .  $K_{p,w}$  and  $K_{p,g}$  represent the consts. of the homogeneous dissociation equil. of water vapor and  $\text{CO}_2$ , resp. From the discussion of the heterogeneous equil. of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  over Fe and its oxides from the standpoint of the phase rule H. concludes that a true chem. equil. does not obtain in a blast furnace. E. R. SCHIERZ.

Transformation points of solid solutions of aluminium oxide and of chromium sesquioxide in iron sesquioxide. H. FORESTIER AND G. CHAUDRON. *Compt. rend.* 180, 1264-6 (1925).—The influence of  $\text{Al}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  on the transformation point of  $\text{Fe}_2\text{O}_3$  at 675° (cf. *C. A.* 19, 1799) is studied in the dilatometer. The hydroxides are pptd. out of aq. solns. of known concn., dried and baked at 500° for 2 hrs. The transformation point is lowered in linear proportion to the added  $\text{Al}_2\text{O}_3$  until 12 mol. % is added and 575° is reached, then it stays const.  $\text{Cr}_2\text{O}_3$  lowers in linear proportion to 220° and 40 mol. % and from there with decreasing magnitude. J. OLY T. STEVENS.

The principles of the temperature measurement and the German law about the temperature scale. F. HENNING. *Z. ges. Kälteindustrie* 32, 4-8 (1925).—The temperature scale of the German Law of August 7, 1924 (*Reichsgesetzblatt Teil I* Nr. 52, 1924), is based upon the second law of thermodynamics. The following fixed pts. serve to standardize measuring devices: optical pyrometer (Wien's law), m. p. Au 1063°; thermoclement (Pt, Pt-Rh), same, m. p. Ag 960.5°, m. p. Sb 620.5°, m. p. Zn 419.45°; Pt resistance thermometer, h. p. S 113.60°, h. p.  $\text{H}_2\text{O}$  100°, l. p.  $\text{H}_2\text{O}$  0°, l. p. Hg -38.87°, b. p.  $\text{O}_2$  -183.0°. The interpolation equation for the thermoclement is  $e = a + bt + ct^2 + dt^3$ ; for the Pt resistance thermometer above 0°  $R = R_0(1 + at + bt^2 + ct^3)$  and below 0°  $R = R_0(1 + at + bt^2 - 5 \times 10^{-12} t^5)$ . OSCAR PAUK.

Heats of formation of aqueous solutions of hydrogen chloride and ammonia at different temperatures. M. VRETSKIY AND N. SAVARITSKIY. *Z. physik. Chem.* 112, 59-6 (1924).—Heats of soln. and diln. have been detd. at various temps. The results obtained are more complete than those of Thomson and of Berthelot. The heats of formation of very concd. solutions vary considerably with the concn., but the variations are relatively small when dil. solns. are formed. At const. temp., the

mol heat of soln of  $\text{NH}_3$  is practically const over a large concn interval. The mol heat of soln of  $\text{HCl}$  increases with rise of temp, while that of  $\text{NH}_3$  decreases.

B. C. A.

Note on the connection between the specific heat  $C_v$ , the inner energy  $U$  and the equation of state of the substance, based on the second law of thermodynamics. H. HAUSEN *Z. Physik* 30, 277-9(1924).—H. shows that Jazyna's proof (*C. A.* 18, 3135) is faulty and his supposed theorem false.

F. R. B.

The proof and basis of the reciprocal theorem. WITOLD JAZYNA. *Z. Physik* 30, 372-5(1924).—Polemical. Cf. Hausen, preceding abstract.

F. R. B.

The physical basis of the reciprocal theorem. W. JAZYNA. *Z. Physik* 30, 376-9(1924), cf preceding abstract.

F. R. B.

The entropy of gases and the theory of quanta. The chemical constant of monatomic gases. A. SCHIDLDF *Arch. sci. phys. nat.* 6, Supplement, 61-7(1924); cf *C. A.* 19, 1089.—I. In classical mechanics the expression of the probability of the state of a system is independent of the form of the cells of equal probability, according to Liouville's theorem, but this theorem cannot be applied to the quantum theory, where the size of these cells is defined in advance as  $h^3$ , where  $h$  is Planck's const. If  $q_1, q_2, q_3$  are the coordinates, and  $p_1, p_2, p_3$  the generalized impulses of a monatomic mol, then  $h^3 = \iiint dp_1 dp_2 dp_3 dq_1 dq_2 dq_3$ . The triple integral  $\iiint dp_1 dp_2 dp_3 dq_1 dq_2 dq_3 = \nu$  signifies the vol in which occurs the quantized movement of the mol. O. Sackur assumes that this vol is  $\nu = V/N$  for a gas composed of  $N$  mols contained in a receptacle of capacity  $V$ . If  $V$  is sufficiently large, the mol behaves as one of the systems of 3 degrees of freedom of a canonical distribution of Gibbs, of modulus  $kT$ , where  $k = R/N$  = gas const divided by Avogadro's no. This distribution is shown to lead to the equation,  $\psi = -kT \log \{V(2\pi kmT)^{3/2}/h^3\} + \epsilon_0$ , where  $\psi$  is the free thermodynamic energy of the mol. From the thermodynamic formula  $S = \partial\psi/\partial T + c$  the equation for the entropy is  $S = k \log \{V(2\pi kmT)^{3/2}/h^3\} + 3k/2 + \text{const.}$  Further equations are developed which are shown to lead to 2 conclusions: (a) The mol movement of progression is to be quantized in the interior of the entire vol of the receptacle which contains the gas; (b) the idea of the abs. entropy gives rise to some difficulties, which disappear, however, if one completes the expression for the entropy by adding a const. II. If  $\gamma$  is the latent heat of vaporization of the mol,  $\log p = -\lambda/kT + \log \{(2\pi m/h^2)^{3/2}/kT\}^{1/2}$  from which it follows that the chem. const. of a monatomic gas has the value  $\log \{(2\pi m/h^2)^{3/2}/kT\}^{1/2}$ .

H. G.

Electronegative potential series in liquid ammonia. F. W. BERGSTRÖM *J. Am. Chem. Soc.* 47, 1503-7(1925).—By chem. methods (replacement of one element by another) the following series has been established for solns in liquid  $\text{NH}_3$  with homoat anions:  $\text{Pb}, \text{Bi}(\text{?}), \text{Sn}, \text{Sb}, \text{As}, \text{P}(\text{?}), \text{Te}, \text{Se}, \text{S}, \text{I}$ . In this, an element will in general displace any element to the left of it. The reactions are briefly described. B. H. C.

Reversible oxidation-reduction in organic systems. MANSFIELD CLARK. *Chem. Reviews* 2, 127-78(1925).—Summary largely of C's work and that of Conant.

G. L. CLARK

Influence of neutral salts on the potential of the hydrogen electrode in contact with a hydrochloric acid solution. L. MICHAELIS AND M. MIZUTANI *Z. physik. Chem.* 112, 68-82(1924).—The change of activity of the  $\text{H}^+$  ions in very dil.  $\text{HCl}$  soln, as influenced by the addn of neutral salts, was examd. by a modification of a method previously used (*C. A.* 15, 1427; 18, 1940). In general, with increasing salt concn, the potential difference rises to a max. in the region 0.2-0.3  $N$ , and then falls, so much so in some cases that the soln. would appear to be more "acid" in the presence of salt than alone. From the results obtained with the alkali chlorides the effect of the different alkali ions is correlated systematically with at. wt. Data are also given for the effect of various mixts. of chlorides on 0.01  $N$   $\text{HCl}$ .

B. C. A.

The technic of series measurements with the gas chain. E. WÖHLISCH. *Biochem. Z.* 153, 129-30(1924).—A satd soln of  $\text{KCl}$  in a round-bottom or Erlenmeyer flask does not creep over the top and sides. Therefore, app. is devised for use with the calomel electrode, with a small Erlenmeyer flask as a salt bridge. The gas electrodes are so arranged that they may be clamped to a vertical metal stand, through which the current is passed. For insulation the whole is placed on a glass plate. An arrangement for shaking the entire stand with the electrode vessels is described. W. D. L.

Potentiometric measurement of the reduction of iodate and periodate by iodide ion. ERICH MÜLLER AND DIETRICH JÜNCK *Z. Elektrochem.* 31, 200-6(1925).—From a study of the titration of iodate with iodide and iodide with iodate in  $\text{HCl}$  of various concns and  $\text{H}_2\text{SO}_4$ , it is concluded that the  $\text{H}_2\text{SO}_4$  soln is to be recommended. The end point (a break in the curve millivolt-cc.  $\text{KI}$  or  $\text{KIO}_3$ , resp.) in  $\text{HCl}$  is markedly

affected by the concn. of the acid. In certain concns. a break occurs at a point representing  $2/3$  of the I required for the equation  $\text{IO}_3^- + 6\text{H}^+ + 5\text{I}^- \rightarrow 3\text{I}_2 + 3\text{H}_2\text{O}$ . This is due to the formation of  $\text{ICl}$ . At still higher concns. of  $\text{HCl}$  the break does not occur at the true end point because of the escape of  $\text{Cl}$ . In the titration of the periodate with iodide as well as in the reverse titration  $\text{H}_2\text{SO}_4$  is to be preferred for the reasons given above. Accurate results can be obtained in 0.003 *M* solns. For the more rapid differential method the values for transition potential are +0.58 v and +0.60 v (against normal electrode) for iodate and periodate, resp. E. R. SCHIERZ

Potentiometric measurement of the reaction between chlorine and iodide ion. ERICH MÜLLER AND DIETRICH JUNK. *Z. Elektrochem.* 31, 206-9 (1925).—In the titration of chlorine water with  $\text{KI}$  soln., measured potentiometrically, two breaks occur in the curve. (cf. preceding abstr.) These breaks indicate that the reaction occurs in steps (1)  $3\text{Cl}_2 + \text{I}^- + 3\text{H}_2\text{O} = \text{IO}_3^- + 6\text{HCl}$  (2)  $\text{IO}_3^- + 5\text{I}^- + 6\text{HCl} = 3\text{I}_2 + 3\text{H}_2\text{O} + 6\text{Cl}^-$ . In the presence of  $\text{HCl}$ , however, another break occurs when  $1/2$  the  $\text{KI}$  necessary for equations 1 + 2 has been used. This indicates the following reactions: (3)  $3\text{Cl}_2 + \text{I}^- + 3\text{H}_2\text{O} = \text{IO}_3^- + 6\text{H}^+ + 6\text{Cl}^-$ , (4)  $\text{IO}_3^- + 2\text{I}^- + 3\text{Cl}^- + 6\text{H}^+ = 3\text{ICl} + 3\text{H}_2\text{O}$ ; (5)  $3\text{ICl} + 3\text{I}^- = 3\text{I}_2 + 3\text{Cl}^-$ . In the presence of  $\text{H}_2\text{SO}_4$  the reaction proceeds as in the absence of acid but the breaks are more marked. In titrating  $\text{KI}$  soln. with chlorine water again two breaks are observed, which correspond to those obtained above. In the presence of  $\text{HCl}$  an intermediate break occurs which is accounted for by the formation of  $\text{ICl}$ . In the presence of  $\text{H}_2\text{SO}_4$  the reaction proceeds as in the absence of acid. The iodine color disappears before the end point is reached; this may also be due to the formation of  $\text{ICl}$ . E. R. SCHIERZ

A new phenomenon in the diamagnetism of gases. A. GLASER. *Ann Physik* [iv], 75, 459-88 (1924); *Physik. Z.* 26, 212-7 (1925).—The susceptibilities of  $\text{H}_2$ ,  $\text{N}_2$ , and  $\text{CO}_2$  were measured at pressures varying from a few mm. to 900 mm., and for field strengths up to 4,500 gauss. The method consisted essentially in measuring the turning moments exerted on a small cylindrical specimen of paramagnetic material, suspended by a quartz fiber in a magnetic field, when surrounded by the gas under examn. and when the gas was completely exhausted. Special precautions were taken to insure constancy of temp. and of magnetic field during the measurements. The strengths of the fields were measured by a Bi spiral, and pressures by a special Hg manometer. The results are given only in the form of pressure-susceptibility diagrams. These indicate that, as the pressure is increased, the susceptibility increases in direct proportion up to a certain point. The curves then bend smoothly but rapidly and finally at a certain critical pressure again become practically straight lines. In this second stage the increase of susceptibility with pressure is less rapid than in the first. The values of these critical pressures vary somewhat with field strength; they are approx. 300 mm. for  $\text{CO}_2$ , 350-400 mm. for  $\text{N}_2$ , and 600 mm. for  $\text{H}_2$ . The curves for a given gas, as shown, seem to be practically identical for the various field strengths. Some possible theoretical implications of this phenomenon are discussed. W. W. STIFLER

Albert W. Hull's "magnetron." C. POLYANI. *Nuovo cimento* [N. S.] 2, 75-82 (1925).—Using Hull's expl. data (*C. A.* 15, 3032), P has calcd. values for  $H$  of the magnetic field described. These amount to 50 gauss (deduced from the curve) and 74.8 gauss calcd. from the relation  $\bar{H} = \sqrt{8\pi} \epsilon \sqrt{V/R}$ . Furthermore it is possible to calc. from these data that the e. m. f. of induction in abs. units has the value  $\Phi$  maxwell/I sec. =  $1.1 \times 10^{-10}$  volts. L. T. FAIRHALL

The study of the relations between molecular constitution and color. MIRCEA V. IONESCU. *Bul. soc. stiinte Cluj* 2, 280-88 (1925).—In expl. verification of Radulescu's electronic theory of selective absorption the absorption spectra of the fulvenes of Thiele were detd. Under the conditions that (1) the structure and nature of both chromogen and substituting radical were entirely defined and excluded tautomers, (2) the position of the substituted group is always the same with respect to the chromogen and (3) the introduction of two chromogens into the mol. is made so as to exclude all conjugation, it was found from the study of benzo- and dibenzofulvenes that: (1) The "bathochrome" effect of introduced groups, increases in the order of their chem. activity, that order being const. and independent of the nature of the chromogen, (the derivs. studied were the phenyl, anisyl, furyl, styryl, piperonyl, piperyl, *p*-Mer- $\text{NC}_6\text{H}_4$ , etc.). (2) For the same substituted group, the absorption depends on the nature and structure of the chromogen. The derivs. of benzofulvene absorb more intensively than the corresponding derivs. of dibenzofulvene. (3) The effect of the entry of an active group, with a "positive surface" into an absorbing mol. is always "bathochrome" and independent of the nature of the chromogen. Full data are given. R. L. B.

Metallic fuster. II. W. D. BANCROFT AND R. P. ALLEN. *J. Phys. Chem.* 29,

564-86(1925) —Metallic luster is obtained when sufficient light seems to come from a single surface and there are suitable variations of intensity in space or time. Metals and many sulfides, phosphides, silicides, selenides, tellurides and arsenides are so opaque that reflected light comes from the surface of the crystals. With interference colors the thickness of the film is so slight that the eye does not detect any depth of reflection. With multiple films the luster is metallic only when the observer is far enough away that the thickness of the film becomes negligible. Stereoscopic luster involves primarily a variation of intensity in time though an additional variation of intensity in space is helpful in causing the sensation of metallic luster. Synchronous intermittent lighting of a rotating part colored disk gives everybody the sensation of metallic luster. There seems no reason to suppose that self-luminous substances will not look metallic if they satisfy the regular criteria.

HARRY B. WEISER

Corrections involved in the measurement of small differences in refractive index of dispersive media by means of the Rayleigh interferometer, with special reference to the application of the results to measurements in diffusion. B. W. CLACK. *Proc. Phys. Soc. London* 27, 116-29(1925).

G. L. CLARK

Calculation of optical refractive indices by the logarithmic rule of averages. KARL LICHTENECKER. *Physik. Z.* 26, 297-302(1925) —The logarithmic rule of averages found applicable for the cond. of binary mixts. holds for refractive indices, especially for the system,  $\text{CS}_2$ -methylal. The rule is:  $\log n = v_1 \log n_1 + v_2 \log n_2$  where  $v_1$  is the vol. occupied by component 1. If a vol. contraction occurs a correction must be applied as in the system,  $\text{H}_2\text{O}$ -pyridine, where the results check the rule within the exptl. error, especially closely up to 50% pyridine.

F. O. ANDEREGO

Constitution of  $\text{HNO}_3$  and the nitronium salts formed with  $\text{HClO}_4$  and  $\text{H}_2\text{SO}_4$  (HANTZSCH) 6. Electronic conception of valence and heats of combustion of organic compounds (KHARASCH, SHER) 3.

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## 3—SUBATOMIC PHENOMENA AND RADIOCHEMISTRY

S. C. LIND

Electric forces and quanta. J. H. JEANS. *Nature* 115, 361-8 (1925). —A lecture. FLORENCE N. SCHOTT

Correction of the research: "Test of the classical dispersion formula for monatomic gases and vapors." K. F. HERZFELD AND K. L. WOLF. *Ann Physik* 76, 567-70 (1925); cf. *C. A.* 19, 1223. —When refractivities of the noble gases are calcd. from the classical formula  $n - 1 = [C_1/(\gamma^2 - \gamma^2)] + [C_2/(\gamma^2 - \gamma^2)]$  ( $C_1$ ,  $C_2$  and  $\gamma^2$  are unknown), the results obtained are not compatible with the accuracy of measurements. When, however, these data are calcd. from an empirical formula suggested by Koch, much better agreement is obtained. H. R. MOORE

Electronic conception of valence and heats of combustion of organic compounds. M. S. KILBASCH AND BEN SHEN. *J Phys Chem* 29, 625-38 (1925). —The heat of combustion of org. compds is assumed to be the energy given out when an electron pair shifts from its relatively non-polar position in the org. bond to the relatively polar positions occupied in  $H_2O$  and  $CO_2$ . The no. of possible degrees of polarity,  $i$ ,  $e$ , the no. of possible energy levels in the Bohr sense is supposed to be finite, not infinite as in the older form of the Lewis theory. The differences in the energy of an electron in non-polar bonds and in the polar bonds of the  $CO_2$  type are sub-multiple of 26.05 kg. cal. per mol. per electron. Thus the heat of combustion of liquid satd. hydrocarbons is 26.05  $N$ , where  $N$  is the number of valence electrons in the compd. If 0 is taken as the energy level of an electron in the polar  $CO_2$  and  $H_2O$  type of bond, the electrons in the non-polar C-H, C-C, N-H and conjugate double bonds, are in energy level 1; the electrons in the partially polar bonds C=C, (non-conjugate), C-OH, C-NO, C-NH, (primary), are in energy level  $1/2$ ; the electrons in =C-OH, =C=O are in energy level  $1/4$ ; the electrons in tertiary alcohols, phenols, anilides and acids O-H and N=O are in levels 0- $1/4$ , the data not being sufficient to decide. These formulas have been tested for 278 org. compds, the agreement being most striking. F. R. B.

The long-range particles of polonium. IRENE CURIE AND NUBUO YAMADA. *Compt. rend.* 180, 1487-9 (1925); cf. *C. A.* 19, 1530. —The no. of long-range particles is dependent on the quantity of Po and not on the metal on which the Po is deposited. These rays are not homogeneous but the no. decreases rapidly between 4 cm. and 12 to 14 cm. If the gas is  $O_2$  or  $CO_2$ , there are about 10 long-range particles for  $10^7$   $\alpha$ -particles; in air, there are 30 for  $10^7$   $\alpha$ -particles. From the intensity of the scintillations, it is extremely improbable that these are  $\alpha$ -particles; they are probably H-particles projected by the  $\alpha$ -rays. MARIE FARNSWORTH

The magnetic spectrum of high-speed  $\beta$ -rays of radium B + C. J. D'ESPINE. *Compt. rend.* 180, 1403-5 (1925). —The magnetic spectrum of the  $\beta$ -rays emanating from Ra B + C was photographed. Measurement of the plates revealed the existence of high-speed rays with velocities between 0.998 and 0.638 of the velocity of light. The new results confirm the existence of rays previously noted by others. C. C. KRESS

The absorption of  $\beta$ -rays by matter. GEORGES FOURNIER. *Compt. rend.* 180, 1490-2 (1925); cf. *C. A.* 19, 1530. —The absorption of  $\beta$  rays is extended to Mg, Fe, Ni, Zn and Cd. The linear law is confirmed. With elements of higher at. no. than 50, the phenomenon of absorption is complicated by secondary rays. Using the linear law, the secondary rays can be studied by subtraction from the expression  $\gamma = k(e^{-\mu x} - e^{-\mu' x})$ . Pt, Au, Th and Pb were examd. The coeff. of absorption of the secondary rays is much smaller than that of the primary ones. M. F.

Paschen-back effect in hydrogen. H. FALKENRAGEN. *Z. Physik* 28, 1-10 (1924). —A theoretical discussion of the changes in the Zeeman pattern of the Balmer lines with the application of very intense magnetic fields. B. C. A.

Inverse Stark effect in sodium vapor. R. LADENBURG. *Z. Physik* 28, 51-68 (1924). —The effect of an intense elec. field on the D-line absorption of Na vapor has been studied, under the dispersion of a Lummer-Gehrcke plate. The construction of a Na vapor lamp, designed to emit the D-lines without self-reversal, is described. The light from this lamp passed between 2 plane electrodes maintained at p. ds. of up to 160,000 v./cm., and the space between the electrodes contained Na vapor at pressures of the order of  $10^{-4}$  mm. Observations in directions perpendicular to the lines of force showed that the elec. field shifted both absorption lines equally to the red. The shift of the parallel component of  $D_2$  is greater than that of the perpendicular component and is 0.025 A. U. for 160,000 v./cm. It is proportional to the square of the field strength. The Stark effects here recorded are in agreement with those predicted by the Bohr

**Anomalous dispersion in the field of X-rays.** E. HJALMAR AND M. SIEGBAHN. *Nature* 115, 85-6(1925).—The lattice const. of calcite and gypsum have been compared, a series of spectral lines with wave lengths from 0.7 up to 5.2 A. U. being used. When values of  $d_1/d_2 = \sin \phi_2 / \sin \phi_1$  are plotted against wave length, the graph shows 2 marked discontinuities coincident with the wave lengths of the absorption edges of Ca and S. B. C. A.

**The physical interpretation of X-ray spectra reflected from fatty acids.** L. DE BROGLIE AND JEAN-JACQUES TRILLAT. *Compt. rend.* 180, 1485-7(1925).—X-ray spectra reflected from crystals of the fatty acids show successive orders given by the well-known Bragg formula. But the odd orders are much more intense than the even orders, which is contrary to the behavior of spectra reflected from inorg. crystals. This behavior may be accounted for on the theory that the planes sep. the  $\text{CH}_2$  chains of 2 adjacent mols. are of weak or zero electron density, the  $\text{COOH}$  planes being of high electron density. An analysis is made which shows that in a homogeneous medium a series of equidistant planes of feeble density will diffuse as if they were of high electron density, but at a phase difference  $\pi$ . Thus all the even orders reflected are weakened, while the odd orders are reinforced. C. C. Kress

**The ultra-violet absorption bands of oxygen as dependent on temperature; and a short-wave-length spectrum of iodine.** CHR. FUCHTBAUER AND E. HOLM. *Physik. Z.* 26, 345-9(1925).—The ultra-violet absorption of  $\text{O}_2$  was investigated at various temps. The gas was enclosed in a quartz tube which could be heated in an elec. furnace. A Zn spark in front of the window of the tube served as source. The spectrograms, secured with a quartz prism spectrograph, showed that as the temp. of the  $\text{O}_2$  increased from  $400^\circ$  to  $1050^\circ$  the absorption increased in intensity and that new bands appeared toward the longer wave lengths. In a table are presented the wave nos. of the band heads which were measured. The lines of resolved bands will be published later. The ultra-violet emission spectrum of I, excited in a discharge tube with electrodes, is very rich in lines of which wave lengths are given for about 40 between 2016 A. U. and 1830 A. U. Of these only 4 appear when an uncondensed discharge excites the I vapor. C. C. K.

**The ultra-violet emission spectra of the halogens.** E. B. LUDLAM AND W. WEST. *Proc. Roy. Soc. Edinburgh* 44, 185-96(1924).—The halogens Cl, Br and I were excited in fused quartz tubes with the discharge from a Tesla coil. The tubes were provided with external tin foil electrodes. The spectra emitted under these conditions are bands shaded toward the violet, with max. at wave lengths 320 and 265 m $\mu$  for Cl; 370 and 295 m $\mu$  for Br; and 480 and 345 m $\mu$  for I. Of these the second band is probably the electron affinity spectrum of the halogens, as the values calcd. from them are in fair accord with the theoretical values of the electron affinities. C. C. Kress

**The pole-effect for barium and neodymium lines in the visible part of the spectrum.** J. M. MOHR. *Compt. rend.* 180, 1397-9(1925).—Two bundles of light rays, emanating, resp., from the center and from the neighborhood of the poles of an elec. arc, were passed through an interferometer simultaneously to measure accurately the variations in wave length between the 2 regions of the arc. The sources were C arcs impregnated with the chlorides of Ba and Nd. The salts were placed on the positive electrode. Wave length shifts, or pole-effects, were measured for about 30 Ba lines and 20 Nd lines. The displacements are greatest between the negative pole and the center of the arc and least (practically nil) between the center and the positive pole. C. C. Kress

**Complementary investigations on the structure and distribution of band spectra.** H. DESLANDRES. *Compt. rend.* 180, 1454-60(1925).—The const.  $d_1 = 1062.5$  previously found to occur as a fundamental frequency relating the members of line and band series spectra (*C. A.* 15, 209; 18, 2840) has been found in recent work to be a characteristic frequency in the band spectra of more complex mols. The absorption bands of  $\text{O}_2$ , CO, HCN,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  and  $\text{CH}_4$  can be represented by  $K = q d_1 / rs$ , in which  $s$  is an integer equal to the no. of atoms in the mol. and  $K$  is the const. of the well-known Deslandres formula for band spectra. C. C. Kress

**New lines of lanthanum between  $\lambda$  3100 A. U. and  $\lambda$  2200 A. U. in the spectrum of the arc at normal pressure.** S. PINA DE RUBIES. *Compt. rend.* 180, 1478-80(1925).—Between 3100 A. U. and 2250 A. U. in the ultra-violet about 200 lines were measured in the arc spectrum of La. The material used in the arc was a very pure oxide of La prep. by Urbain. The wave lengths derived from the measurements are presented in a table. C. C. Kress

**Infra-red absorption spectra of aldehydes and ketones.** JEAN LECOMTE. *Compt. rend.* 180, 1481-2(1925).—New observations of absorption spectra between 2.75  $\mu$  and 8  $\mu$  has shown: (1) that the spectra of the fatty aldehydes and their isomeric ketones are not identical; (2) that the characteristic band of the carbonyl group is not the same

for the fatty series as for the aromatic series. The data for the compds investigated are given in a table, from which it is seen that the absorption spectra of the ketones and aldehydes are sufficiently distinct to permit their use in analytical work. C. C. K.

The use of spectroscopes of high resolving power. VASCO RONCHI. *Nuovo cimento* [N. S. 1], 2, No 1, 1-15(1925).—A general discussion of instruments of this type including the application of a diffraction grating, type of illumination, photography, stability of the instrument and effect of unsteadiness. L. T. FAIRHALL.

The (arc) spectrum of iron-carbon mixtures. J. H. REINIERS, JR. *Verslag Akad. Wetenschappen Amsterdam* 33, 655-60(1924).—R. studies the disappearance of the C bands by addn of Fe to the anode. A liquid C-Fe mixt could not be obtained contg less than 75% Fe, and this would not give the  $C_2N_2$  band of C (3885 Å. U.). With mixts of powd C and Fe, this band was visible from 30 to 90% Fe. Most of the other C bands disappear when 2% Fe is added, with the exception of 5152-5159, which can still be detected with 25% Fe. The arc voltage decreases from 86.5 to 39.1 v., and the intensity increases from 2.7 to 3.9 amps., when the percent Fe is increased from 0 to 25%. G. CALINGAERT.

The structure of the ultra-violet bands of water vapor. G. H. DIEKE, *Verslag Akad. Wetenschappen Amsterdam* 34, 100-7(1925); cf. C. A. 19, 1375.—D., using existing data, shows that it is possible to explain the structure of the ultra-violet spectrum bands of  $H_2O$  vapor without making any hypothesis as to the structure of the emitting mol. Also in *Proc Acad Sci Amsterdam* 28, 174-81(1925). G. CALINGAERT.

The arc spectrum of rhodium. L. A. SOMMER. *Naturwissenschaften* 13, 392-3(1925).—A preliminary note on the measurement of some 1500 lines in the rhodium spectrum; 400 could be classified. B. J. C. VAN DER HOEVEN.

Tesla-luminescence spectra. V. Some polynuclear hydrocarbons. Wm. H. McVICKER, J. K. MARSH AND A. W. STEWART. *J. Chem. Soc.* 127, 999-1006(1925); cf. C. A. 19, 11.—The Tesla-luminescence spectra of the following compds with 2 or more isolated benzene rings were examd: diphenyl, diphenylmethane, triphenylmethane, dibenzyl, stilbene and tolane. The following compds with closed rings were also examd: fluorene, acenaphthene, anthracene, phenanthrene, naphthanthracene, 1-methylnaphthalene, 2-methylnaphthalene, 9-phenylfluorene, 9-phenylnaphthalene, 1,2,3,4,5,6,7,8 octahydroanthracene and retene. A description of the spectrum of each compd. is given and the relation between constitution and spectra is discussed. M. F.

The decomposition of nitrous acid in light and in the presence of catalysts. K. B. MUKERJI AND N. R. DHAR. *Z. Elektrochem.* 31, 235-9(1925).—The reaction kinetics of the reversible reaction  $3HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O$  are investigated in both the light and dark. The velocity const. increases with the concn of the  $HNO_2$ , as evidenced by the results,  $K = 0.00129$  in  $N/128$  soln,  $K = 0.00134$  in  $N/64$  soln, and  $K = 0.00135$  in  $N/32$  soln. Decompn. is more pronounced in open than in closed vessels. This is ascribed to the inhibiting properties of NO, which is unable to escape in closed reaction chambers. Since NO exerts an anticatalytic effect on the reaction, due probably to its ability to combine with and reduce  $HNO_2$  (cf. C. A. 5, 2209), M. and D. have studied the influence of various substances which conceivably might be expected to alter its concn. The substances were chosen with special reference to the principle that in all oxidation reactions reducing agents act as negative catalysts. Positive catalysts usually possess the property of combining with the NO ( $KClO_4$ ,  $Ca(NO_3)_2$ ) or removing it by oxidation. The mean value of  $K$  without catalysts was 0.00130; with accelerators this value was increased to 0.00201 with  $Fe(NO_3)_3$ , to 0.00310 with a trace of  $Fe(OH)_3$  sol., to 0.00507 with  $Ca(NO_3)_2$ , and with negative catalysts values of  $K$  intermediate between 0.000727 and 0.000322 for sucrose and  $H_2O_2$ , resp., were obtained. The temp. coeff. of the reaction increases with temp., in agreement with the work of Ray, Ghosh and Dhar (C. A. 11, 2301). This anomaly is a direct consequence of the decreased soly. of the NO at higher temps. and its progressive inability to inhibit the further course of decompn. of  $HNO_2$ . HOWARD R. MOORE.

Studies in the experimental technic of photochemistry. II. The determination of the energy distribution and the total energy in the radiation from quartz mercury-vapor lamps. R. G. FRANKLIN, R. E. W. MAODISON AND L. REEVE. *J. Phys. Chem.* 29, 713-26(1925); cf. C. A. 19, 789.—A thorough photochem. investigation presupposes knowledge of the energy distribution of the various lines emitted by the light source in addition to the total energy. The distribution of energy, for both simple and compd. lines (composed of doublets or triplets), is obtained from curves in which intensity is plotted against wave length. The intensity of any given radiation admitted through a spectrometer and incident on a spectro-thermopile is recorded by the deflections of a Paschen galvanometer. Triangular diagrams provide a basis for the estn. of the

energy in any particular line, and make allowance for the finite width of the collimator slit. Absolute energy is secured from a surface thermopile, calibrated with Hefner lamps of known energy characteristics. H. R. MOORE

The photosensitive formation of water from its elements in the presence of chlorine. R. G. W. NORRISH AND E. K. RIDEAL. *J. Chem. Soc.* 127, 787-97 (1925).—Weigert (*Ann. Physik* 24, 55, 243) observed the formation of  $H_2O$  in the photochem. synthesis of  $HCl$  when appreciable amts. of  $O_2$  were present, but failed to associate this result with the inhibiting properties of  $O_2$ . A quant. study of the rate of reaction, followed by decrease in pressure in a reaction tube contg.  $P_2O_5$ , leads to the relation  $d[H_2O]/dt = K[O_2][Cl_2]$ . The velocity of combination of  $H_2$  and  $O_2$  is independent of the pressure of the  $H_2$  between the limits 0.16 to 0.9% of the total pressure. The decrease of pressure per unit time is estd. from curves constructed from data obtained for  $[H_2]/[O_2]$  ratios of 4 to  $1/4$ , and for  $Cl_2$  in varying proportions. The reaction is cited as an example of photochem. sensitization (cf. *C. A.* 17, 2392). The transference of intra-at. energy from active  $Cl$  mols. to  $O$  presumably elicits formation of active  $O$ , which reacts with  $H_2$  to give  $H_2O$ . H. R. MOORE

The photochemical decomposition of chlorine water and of aqueous hypochlorous acid solutions. I. A. J. ALLMAND, PERCY WALMSLEY CUNLIFFE AND R. E. W. MADDISON. *J. Chem. Soc.* 127, 822-40 (1925).—The photolysis of aq.  $Cl_2$  and  $HOCl$  is considered from the point of view of the equation  $Cl_2 + H_2O \rightleftharpoons HClO + H^+ + Cl^-$  and the Jakowkin equil. ratio  $[Cl_2]/[H^+][Cl^-][HOCl] = K$  (*Z. physik. Chem.* 29, 621). It is clear from the equil. relations involved, granting that  $Cl_2$ ,  $HOCl$ , or  $ClO^-$  is the photosensitive substance, that any agents removing the products of the decompn. will accelerate the forward reaction. Accordingly in  $Cl_2$  solns. the effect of increasing and suppressing the  $[Cl^-]$  was studied by adding in the first case  $LiCl$ ,  $KCl$ ,  $CdCl_2$ ,  $HCl$ ,  $H_2SO_4$ , the neutral salts  $Na_2SO_4$  and  $Li_2SO_4$ , and in the second case  $HgCl_2$ , which reduces the  $[Cl^-]$  by the formation of  $HgCl_2^{--}$ . The rate of formation of  $HClO_2$  was taken as an index of the quant. extent of change, although  $O_2$  is also one of the major products. No  $HClO_2$  nor  $H_2O_2$  is produced, contrary to the statements of other investigators. In  $HgCl_2$  solns. the quantity of  $HClO_2$  developed is 64.1% of the total  $Cl_2$  present, an appreciable increase when compared with yields of 56% in  $HCl$  solns. and 62% in  $KCl$  solns. With solns. of  $HOCl$ , 61% of  $HClO_2$  was developed on exposure to light. This ratio was increased considerably when salts capable of removing  $H^+$  were added to the acid. For 0.25 *M*  $Na_2HPO_4$  the yield was 81%, and for 0.125 *M*  $Na_2HPO_4$ , 86%. The theory advanced for both reactions is that  $HOCl$  acts as an acceptor for  $O$  atoms formed in the light. Thus  $HClO_2$  is the end product of the photolysis. Neither reaction exhibits marked selectivity with respect to wave length; sunlight, diffused daylight and the lines  $\lambda 313$ , 365 and 436 $\mu$  are equally effective. H. R. M.

The reaction of ketones with alcohols under the influence of light. J. BÖSEKEN, W. D. COHEN AND S. L. LANGEDIJK. I. The absorption spectra of some ketones. S. L. LANGEDIJK. *Rec. trav. chim.* 44, 173-91 (1925).—After a general introduction and review the data and graphs for the absorption spectra of benzophenone (I), fluorenone (II) and terephthalophenone (III) are given. The absorption of these compds. was detd. and compared in the boundary region between the visible part and the ultra-violet part of the spectrum (3600-4500 Å. U.). The absorption of I melted and in  $EtOH$  solns. of various concns. and of II and III in  $EtOH$  solns. of various concns. and in petroleum ether were detd. From the data conclusions can be drawn concerning several questions relative to the purpose for which this photochem. study was undertaken. These conclusions and their discussion will be reserved until the remainder of the work is published. It was found that neither the absorption of benzophenone nor that of the other ketones examd. gives a max. in the chemically active region. The absorptions measured may be considered as the continuation of the bond which has its max. in the ultra-violet; for II the agreement is practically perfect. Plotnikov's law (*Allgemeine Photochemie*, p. 54-5 (1920)) is not confirmed by these results since the ultra-violet light of max. absorption does not activate the reaction. E. J. WITZEMANN

The M-series of tungsten. ROBERT THORAEUS. *Z. Physik* 26, 396-9 (1924); cf. Siegbahn and Thoraeus, *C. A.* 19, 1987.—Of the 17 lines in the M-series of W predicted by theory, 13 are found, a celluloid window and a crystal of palmitic acid being used. Some of the lines are very faint so that the 4 missing lines may not have produced sufficient blackening to be developed in the photograph. The definition of the lines is improved by stretching the crystal of palmitic acid. D. C. BARDWELL

Double decompositions of siloxene with halogen compounds and their initiation by light (KAUTSKY, THRELE) 6.

ANDRADE, E. N. DA C. *The Structure of the Atom.* London: G. Bell & Sons, Ltd. \$4 14.

JOLY, JOHN. *Radioactivity and the Surface History of the Earth.* Halley Lecture, May 1924. London. Oxford University Press. 40 pp diagrams. Maps. \$1 35. Reviewed in *Mech Eng* 47, 525(1925).

X-ray apparatus. W. COOLIDGE. U. S. 1,543,654, June 23.

#### 4—ELECTROCHEMISTRY

COLIN G. FINK

Electrometallurgical method of manufacturing alloy steel and ferro alloys. ANON. *Teknisk Tidsskrift* 7, 9-15(1925). C. G. F.

The electric furnace in the foundry. ANON. *Elec. Rev.* 96, 515-6(1925). C. G. F.

Combining the retort process with electric smelting of zinc ores. R. W. HALE. *Eng. Mining J. Press* 118, 375-7(1924).—In the Johnson-Hale duplex process 50-75% of the Zn in the ore is extd by retorting at 1150° for 12 hrs. The remaining charge is then transferred to an elec. furnace and raised to 1300° to recover Zn, Pb, Cu, Au and Ag. This operation requires about 400 kw.-hrs. per ton of ore; the electrode consumption is 7-10 lb. per ton of ore. Compared with the present process the fuel for reduction is cut in half, 25% more ore can be charged—retorts are charged twice in 24 hrs., the labor cost is cut to 40%. The charge is never worked to the point where the retorts might be damaged by the formation of slags—this stage is passed in the elec. furnace. The "blue powder end" of the present process is eliminated; a 90% condensation instead of only 65% is possible. The slag losses are reduced to 40 lb. Zn per ton as against 120-160 lb. with the retort process. A. D. SPILLMAN

New methods of manufacturing electrolytic iron. ANON. *Elektrotech. Maschinenbau* 43, 143-4(1925).—A review. C. G. F.

The action of gelatin in the electrodeposition of cadmium. E. MULLAU. *Bull. soc. chim. Belg.* 34, 143(1925).—M. points out that addn. of gelatin will produce smooth coherent deposits of Cd only if the Cd salt of a strong acid ( $H_2SO_4$ ,  $H_2SiF_6$ ) is being electrolyzed in the presence of an excess of the same acid. If  $AcOH$  is used the gelatin has no effect (cf. *C. A.* 19, 938). WM. B. PLUMMER

Production of electrolytic zinc in America. H. LUNDIN. *Teknisk Tidsskrift* 55, 41-5(1925).—Review of Anaconda and other processes. C. G. F.

Production of electrolytic zinc in France. L. V. *J. four. elec.* 34, 107(1925).—Electrolytic Zn plants are located at Bayonna and at Viviez (Aveyron). The latter has been in operation for some time. The Bayonna plant uses Pyrenites blende as raw material. [No details of process are given.] C. G. F.

Electromotive behavior of aluminium. L. A. SMITH. *Z. Elektrochem.* 30, 423-35(1924).—When a pure Al electrode, previously immersed in an  $Al_2(SO_4)_3$  soln., is transferred to another of the same concn., but satd. also with  $HgCl_2$ , in an atm. of N, its potential first becomes more positive and then more negative than in the original state. At the same time a gray Hg deposit forms on the electrode, and there is probably an equil. set up between a liquid and solid amalgam and the electrolyte soln. After remaining at a max. negative potential for some time, the surface becomes bright, because of the complete covering of the electrode by a liquid amalgam, and the potential begins to fall again. The presence of the Hg makes the Al more active. It therefore dissolves in water, leaving the Hg poorer in Al, and the potential becomes more positive. The whole process takes place more quickly with a polished electrode than with one etched with  $HCl$  and washed with distd. water. It is considered that in the second case  $Al(OH)_3$  acts as a retarder. In the presence of the nitrate ion the action on the polished electrode is retarded, while the potential of the etched electrode remains positive indefinitely, as if no Hg had been pptd. on it. If, however, it is washed and transferred to a pure  $AlCl_3$  soln., it immediately takes on a large negative potential, which increases on keeping. This shows that Hg has actually been present in the electrode and that the nitrate ion has completely inhibited the usual reactions. The electromotive behavior of an Al electrode in aq.  $AlCl_3$  solns. of different H-ion concns. has also been studied. The Al becomes most passive between the H-ion concns.  $10^{-11}$  and  $10^{-12}$  but never behaves as a H electrode, showing that, under the conditions of the expts., the Al is never covered with an insulating film of oxide, but always behaves as a metallic

electrode. The results are explained in accordance with S's views on electromotive equilibria, as deduced from his theory of allotropy. B. C. A.

Electrochemical preparation of theophylline. Y. YOSHITOMI. *J. Pharm. Soc. Japan* No. 510, 649-51(1924).—A new method for the prepn. of theophylline by elec. reduction of 8-chlorotheophylline is given. In a porcelain cup (200 cc. capacity), 90 cc. 50%  $H_2SO_4$  and 5 g. 8-chlorotheophylline are placed, and 75 cc. 50%  $H_2SO_4$  is used as anolyte in a glass tube (500 cc. capacity). With Pb plates as electrodes, 1.5 amp. current is passed for 6 hrs. with stirring at 31-9°. Theophylline thus prepd. is isolated as follows: After the electrolysis, an equal vol. of  $H_2O$  is added to the catholyte and filtered into the cooled filtrate,  $NH_3$  gas is passed. When the filtrate is evapd. to  $1/2$  its vol., a white cryst. substance ppts. out, which m. 264°. An addn. of pure theophylline to these crystals does not alter the m. p. The product contains no halogen, gives the murexide test, and has the compn.  $C_7H_8N_4O_2$ . The % yield is not given. A new type of stirrer to be used during the cooling is described. S. T.

Hydrogen in zinc cathodes. O. C. RALSTON. *Trans. Am. Electrochem. Soc.* 47 (preprint)(1925).—Schwarz (C. A. 17, 2837) describes deposits of Zn which show concentric rings, indicating that the metal has been deposited in layers. The density of Schwarz's metal is 6.9 and on heating, large quantities of H are set free. R. has observed that cathodic deposits of Zn often have well defined warts on the surface, some as large as 4 mm. in diam. These warts usually develop on long standing of the cathodes and their formation is ascribed to the setting free of H, which had been originally co-deposited with the Zn. Unless ways can be devised for preventing the presence of H in cathodic Zn deposits, these may become defective during the course of a year or so by this wart formation. C. G. F.

Theory of the corona of high-tension lines. RAGNAR HOLM. *Wissenschaft. Veröff. Siemens* 4, 14-24(1925). C. G. F.

Measuring the corona of high-tension lines. R. HOLM AND R. STÖRMER. *Wissenschaft. Veröff. Siemens* 4, 25-32(1925). C. G. F.

High-voltage test room designed for safety. ANOV. *Elec. World* 85, 1406(1925); 1 illus.—Description of the test room of the Western Electric Company. C. G. F.

Electric enameling furnace (U. S. pat. 1,542,278) 19.

BILLITER, J.: Die technische Chloralkali-Elektrolyse. 1st ed. Dresden and Leipzig: Theodor Steinkopff. 80 pp. Price, paper, G. M. 2.50. Reviewed in *Ind. Eng. Chem.* 17, 767(1925).

LEBEAU, P.: Four Electrique et Chimie. Paris: R. Pitaval. 600 pp. profusely illus. 66 franc. Reviewed in *J. four Elec.* 34, 112-3(1925).

Storage battery. J. M. LEA. U. S. 1,543,017, June 23. Structural features.

Dry batteries. C. S. RIDER. U. S. 1,542,911, June 23. Structural features.

Dry battery. H. M. KORETZKY and B. H. TEITELBAUM. U. S. 1,542,705, June 16.

Electrolytic cell. H. I. ALLEN. Can. 247,513, Mar. 10, 1925.

Electrolytic cell adapted for purifying water. F. E. HARTMAN and H. B. HARTMAN.

U. S. 1,541,947, June 16.

Electric arc and resistance furnace for melting ores and metals. T. LEVOZ. U. S.

1,542,562, June 16.

Treatment of lead-zinc sulfide ores. E. A. ASHCROFT. Can. 247,418, Mar. 10, 1925. S is expelled from the ore, the metals are extd. as chlorides and electrolyzed to recover the metals and Cl. The  $PbCl_2$  is sepd. from the other chlorides with cold concd.  $ZnCl_2$  soln. and the insol.  $PbCl_2$  is sepd. and dried for electrolysis.

Electrodeposition of chromium. R. GRAH. U. S. 1,542,549, June 16. See Brit. 223,611 (C. A. 19, 1101).

Improving electrolytic copper. S. SONORA. U. S. 1,543,237, June 23. The phys. properties of electrolytically deposited Cu sheets are improved by annealing at 300-800° for 5 min. or longer, rolling at a circumferential speed of not more than 450 ft. per min. and pickling with dil.  $H_2SO_4$ .

Discharging electrolytic metal baths, particularly aluminium. AKTIESELSKAPET NORSKE ALUMINIUM COMPANY. Norw. 41,060, March 9, 1925. The liquid metal is tapped directly into a refining spout from which it runs through overflows into a series of ingot molds connected mutually by overflows. Cl. C. A. 19, 613.

Electrolytic hydrogen and oxygen production. E. BAUK. U. S. 1,543,357, June 23.

Molten NaOH or KOH (or a mixt. of both) contg. H<sub>2</sub>O is electrolyzed with high c. ds. and the H<sub>2</sub>O is replaced as consumed. An app. is described.

Self-burning electrodes. **DET NORSKE AKTIESELSKAP FOR ELEKTROKEMISK INDUSTRI** Norw. 41,050, March 9, 1925. The electrode is provided with a metal mantle which is removed successively as soon as the corresponding part of the electrode has obtained the necessary strength by the burning, in order that the metal of the mantle shall not contaminate the fusion.

Electrodes for photoelectric cells, etc. **W. O. SNELLING**. U. S. 1,543,033, June 23. A film of Au is carried by a gauze of metal wire or other conductive material.

Thermionic cathode. **J. E. HARRIS**. U. S. 1,512,385 June 16. Electron-emitting cathodes comprise Pt, Ni, Ba oxide and Sr oxide.

Electrolytic condensers, rectifiers and lightning arresters with filmed electrodes. **R. D. MERRISON**. U. S. 1,543,225, June 23. Structural features.

Cement for incandescent lamps. **W. C. ISLER**. Can. 247,120, Feb. 24, 1925. A C filament is united to a leading-in wire with finely divided graphite suspended in a liquid.

## 5-PHOTOGRAPHY

C. E. K. MEES

Photochemical studies. IV. The properties of the silver gelatino-halides. **A. REICHLER**. *Bull. soc. chim. Belg.* 33, 550-6(1924); cf. *C. A.* 18, 1090, 1248—A large no. of expts. have been carried out by adding 2 cc. of approx. 0.1 N soln. of alkali halides to 10 cc. of a 1% gelatin soln., 2 cc. of 0.1 N AgNO<sub>3</sub> being then added under varying conditions (of lighting during the addn., after it, etc.), and finally a metal  $p\text{-C}_6\text{H}_4(\text{OH})_2$  developer added under various conditions. Coagulation of the colloidal AgBr solns. prepd. as above is accelerated by light or NH<sub>3</sub>. Although the freshly prepd. colloidal AgBr is not readily attacked by the developer, if coagulation has started before the addn. of developer its action is rapid. This is explained on the basis of partial decompos. during coagulation, the metallic Ag particles thus produced forming elec. couples with the AgBr particles to which they are attached, and the action of the developer is thus facilitated. Analogies are drawn between the exptl. results and the observed behavior of AgBr in photographic emulsions. **WM. B. PLUMMER**

Subhalide and germ theory of the latent photographic image. **A. STEIGMANN**. *Camera (Lucern)* 3, 189-92(1925).—S seeks to reconcile the germ theory of the latent photographic image with a modified subhalide theory, and suggests that a Ag nucleus formed either by reduction or by exposure may exert a disorienting influence on the regular space lattice of the Ag halide, because of residual valencies of the nucleus. A very labile crystal form of Ag halide may result, which need not differ chemically from the original Ag halide. The formation of a latent image by heat and abrasion may be due to a modification of the crystal form of the Ag halide. Heat and pressure may cause a more easy reduction of the Ag halide to result from naturally present irregularities on the space lattice. Fragments of the space lattice may be present, in which one Ag atom, instead of being surrounded by 6 Cl atoms, may be accorded only 5, 4 or 3.

M. W. SEIMOUR

The use of commercial plates in research on the latent photographic image. **F. C. TOV**. *Phil Mag* 49, 1104-12(1925).—In single-layer plates the no. of developable centers are greater for light which is more absorbed by the photographic plate. For thickly coated plates this differential absorption leads to the conclusion that while for low exposures the photographic effect is greater for the more strongly absorbed light, as in a single layer plate, for larger exposures a point is reached where the photographic effect is the same, and for even larger exposures the less absorbed light has a greater photographic effect. Conclusion Helmholtz's results on the no. of quanta necessary to render developable a single grain of Ag halide are meaningless, and present results indicate that all frequencies of ultra violet are equally efficient in making developable the Ag halide grain. **V. C. HALL**

Principles of gold toning. **P. FORMSTECHER**. *Camera (Lucern)* 3, 193-5, 217-9, 239-42(1925), cf. *C. A.* 18, 1954.—Solns. of com. AuCl<sub>3</sub> contain free HCl which attacks the half tones of a print. A AuCl<sub>3</sub> soln. neutralized with CaCO<sub>3</sub> turns colorless because the AuCl<sub>3</sub> is converted, by the trace of alkali, into AuCl. For the same amt. of Ag attacked aurous salts deposit more Au than auric salts. Neutral and alk. Au baths give blue tones, while acid baths give red tones. The acid prevents coagulation of the Au to a blue deposit. NaCl improves the keeping qualities of the prints. When it is used with a Au toning bath

it renders toning slow and incomplete, but when used for washing self-toning papers, it gives bluer tones than plain  $H_2O$ .  $KBr$  acts similarly to  $NaCl$ , but to a more marked degree.  $KI$  can be used in  $Au$  toning baths only if the  $Au$  is present in a complex. A solvent for  $Ag$  salts, such as thiocyanate, in a  $Au$  toning bath permits more rapid and complete toning. Thiosulfate added to a  $Au$  soln. constitutes the ideal toning bath if the formation of  $Ag_2S$  can be prevented.

M. W. SEYMOUR

**Sulfur and selenium toning of photographic developing-out paper.** A. STEIGMANN. *Camera (Luzern)* 3, 233-5 (1925).—Prints toned completely with  $Se$  may be treated in the following bleach bath.  $H_2O$  100 cc.,  $K_2Fe(CN)_6$  3-6 g.,  $KBr$  1-2 g.,  $KI$  0.5 g. The almost black  $Ag_2Se$  image thereby changes its color from brown to reddish. Two chemical changes take place: (1) The  $Ag$  and  $Se$  are sepd. with the formation of  $AgBr$  and  $AgI$  and free  $Se$ ; (2) the  $Se$  is oxidized to yellowish red  $Se_2I_2$ . Prints so bleached, when exposed to light, take on a purple-brown-gold tone that is fairly light-stable. Prints that do not change in the light may be obtained by adding  $Na_2S_2O_5 \cdot 5H_2O$  to the bleach bath, or by subsequently fixing the prints. A somewhat more irksome toning process which is justified by the beauty and variety of the tones obtainable consists in toning  $Ag_2S$  images with  $Se$ , followed by  $Au$ . Red to black tones may be obtained, depending upon the time of treatment in the  $Se$  bath.  $Ag_2S$  gives, with  $Au$  salts, a red ppt. of pure  $Au$  gel, presumably according to the equation  $4NaAuS_2O_3 + 2Ag_2S + 2H_2O + 3O_2 = 4Au + 4NaAgS_2O_3 + 2H_2SO_4$ . The longer the  $Se$  treatment, the less  $Ag_2S$  remains, and the browner or blacker is the tone obtained on subsequent toning with  $Au$ .  $Au$  toning may be used as a qual. test to det. whether toned images consist of  $Ag_2S$  or  $Ag_2Se$ .

M. W. SEYMOUR

**Practice of bright light development.** A. HÜBL. *Camera (Luzern)* 3, 213-5 (1925); cf. following abstr.—Yellow safe lights for bright light development by means of desensitizers must absorb both blue and blue-green light. Orthochromatic plates bearing a yellow dye, and especially plates with a colored sub-coating, are often desensitized very slowly. A 32, or 50, c. p. light may be used behind the red filter, giving an illumination of about 20 meter candles at a distance of 50 cm. Where a slow developer is used, H. recommends adding the desensitizer to the developer. When the time required to desensitize is long compared with the development time, desensitizing in a preliminary bath of pinakryptol yellow is recommended. Since its desensitizing action is destroyed by developers, some pinakryptol green should be used in the developer. Pinakryptol is a mixt. of pinakryptol yellow and pinakryptol green.

M. W. SEYMOUR

**Development by bright light.** A. HÜBL. *Phot. Korz.* 61, 4-6 (1925).—A new desensitizer, called Pinakryptol Green Th., has been found by the Hoechst dye works. It is a deriv. of pinakryptol green, but when used in the same concn. is 40 times as powerful a desensitizer as pinakryptol green. One g., dissolved in 100 l. of  $H_2O$ , desensitizes so thoroughly that a plate may be developed in bright yellow light. A discussion of the use of desensitizers, in general, is given. Cf. preceding abstr.

M. W. S.

**Manufacture of photographic developers. III. Preparation of *p*-aminophenol sulfate from  $\beta$ -phenylhydroxylamine.** M. HORII and K. KUMORI. *Report Osaka Ind. Research Lab. (Japan)* 5, No. 13, 1-21 (1924).—Since H. and K. can now prep.  $\beta$ -phenylhydroxylamine easily from nitrobenzene by reduction with acidified  $Na_2S$ , a cheaper method of prepn. of *p*-aminophenol is attempted. The best conditions for mol. rearrangement of  $\beta$ -phenylhydroxylamine to *p*-aminophenol by dil.  $H_2SO_4$  are investigated. **Conclusions.**—To obtain the max. yield, large excess of 3 *N*  $H_2SO_4$  must be used. If *p*-aminophenol sulfate is to be obtained, the use of 4.5 l. of 2 *N*  $H_2SO_4$  for each 327 g. of  $\beta$ -phenylhydroxylamine is the best (73.0% yield). The rearrangement is best above 70°; the yield decreases considerably at 60° because of formation of azoxybenzene; 20 min. heating is sufficient. The method of estn. of the various by-products as well as the aminophenol, sepn. of this final product, and the cost of manuf. of this ingredient of the developer are given in detail.

S. T.

**Keeping property of developing agents.** P. STRAUSS. *Phot. Ind.* 1925, 309-12.—Exhaustion tests were made with 14 different solns. made from 12 different developing agents. The general formula consisted of the developing agent in 0.05 *N* concn., 35 g. per l. of  $Na_2SO_3$  and 35 g. per l. of  $K_2CO_3$ . *H* & *D* curves were plotted at various stages of exhaustion, a motion picture positive film being used. As a result of these tests the developers were placed in the following order in respect to their resistance to exhaustion: metol, metol hydroquinone, *p*-aminophenol, metol adurol, rodinal edinol, ortol, adurol, glycine, amidol, pyrocatechin, hydroquinone, eikonogen, pyrogallol.

M. L. D.

**Application of formalin. I. A new method of *p*-hydroxyphenylglycine synthesis.** KOTARO SUMO. *Report Osaka Ind. Research Lab. (Japan)* 5, No. 7, 1-13 (1924).—To find a cheaper method of prepn. *p*-hydroxyphenylglycine for photographic use, the

following synthesis is devised. Dissolve 30 g. *p*-aminophenol-HCl in 140 cc. hot  $H_2O$ , and add 17 cc. conc. formalin, while cooling with ice water. During continuous cooling and stirring add 75 g. KCN soln. (20%) in drops. A 95% yield of crude  $HOC_6H_4NHCH_2CN$  is formed, it can be purified with hot water and charcoal. If exactly the same amt. of formalin is added after an addition of KCN the yield is 82%. If the free base is mixed with glacial AcOH, and KCN and formalin are added alternately in small quantities at a time, and heated for 30 min. at  $70-80^\circ$ , 89% of the nitrile is obtained. The nitrile thus obtained contains no  $H_2O$  of crystn. Dissolve 20 g. of the nitrile in 100 cc. 10% KOH and 50 cc.  $H_2O$  and boil for 15-20 min. till no more  $NH_3$  is given off. On neutralization with dil. HCl, and acidulation with AcOH, *p*-hydroxyphenylglycine ppts. out in 84.2% yield. The methods of prepn. of Ac and Et derivs. of *p*-hydroxyphenylglycine and their properties are also given. S. T.

**Mercury print.** A new commercial printing process. A. STEIGMANN. *Camera (Luzern)* 3, 215-6(1925).—A well sized paper is coated with Eder's photometer soln. prepd. as follows: 4 g. of  $(CO_2H)_2 \cdot 2H_2O$  are dissolved in 100 cc. distd.  $H_2O$ ; 5 g. of  $HgCl_2$  are dissolved in the same amt. of  $H_2O$ ; 50 cc. of the  $(CO_2H)_2 \cdot 2H_2O$  soln. are mixed with 25 cc. of the  $HgCl_2$  soln.; 1 drop of  $FeCl_3$  is added.  $NH_4OH$  is added drop by drop until a slight cloudiness is produced. A few drops of  $(CO_2H)_2 \cdot 2H_2O$  soln. are then added. The soln. so prepd. is ready for coating. The coated paper is dried in the dark. Exposure is made by sunlight and development is carried out in a phys. Hg developer such as Lumière's Hg intensifier. After drying, the print is rather flat. Subsequent toning of the print, or the employment of a contrasty negative, is recommended. M. W. SEYMOUR.

**Fog formation by oxidizing agents.** LÜPPO CRAMER. *Phot. Ind.* 1925, 291.—It has been observed that very weak acids, or very dil. strong acids, fog only emulsions prepd. by the  $NH_3$  process, or which have been previously treated with alkali. A soln. contg. bromide and an acid or oxidizing agent fogs much more intensively than acid alone and affects even neutral ripened emulsions. An example is 2% KBr and 0.2%  $H_2SO_4$ , HCl, or chromic acid. One % quinone soln. contg. KBr destroys a latent image and fogs high-speed emulsions as does persulfate and bromide. Strong acids if used in sufficient concn., fog emulsions which have not been treated with alkali, but if too concd. they cause reversal. All these fogging effects are diminished by desensitizers but not by their leuco bases. M. L. DUNDON.

**The leptology of the silver bromide grain.** T. THORNE-BAKER. *Brit. J. Phot.* 72, 248(1925).—Samples of AgBr prepd. in various ways, (1) direct pptn. in  $H_2O$ , (2) pptn. from  $NH_3$ -AgNO<sub>3</sub>, and (3) emulsified in gelatin, all show the same crystal structure by X-ray examn. AgBr pptd. in the presence of iodide, so-called iodo-bromide of Ag, shows no indication of the presence of AgI. It is, therefore, suggested that in the sensitive emulsion the AgI is adsorbed in colloidal form on the surface of the AgBr grains, and some of the AgI may play a profound part in the ultimate sensitization of the grains. The exact similarity in crystal structure of AgBr over a very wide range of sensitivity leads support to the theory that sensitization is due to substances deposited on the crystal surface. R. B. WILSEY.

**Regenerating worn cinematographic films.** P. J. J. STOCK. U. S. 1,543,301, June 23. The damaged emulsion side of a worn or aged film is treated with a solvent such as warm dil. HOAc or citric acid soln. contg. a tanning agent which will penetrate and swell the material, the swelled material is superficially liquefied by the action of a hot fluid such as steam or hot air and the film is then dried and rehardened.

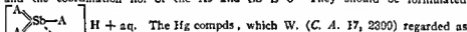
## 6—INORGANIC CHEMISTRY

A. R. MIDDLETON

**Amphoteric oxyhydrates, their alkaline solutions and solid salts (isopolyacids and their salts).** II. The tantalum acids and some of their alkali salts. G. JANDER AND H. SCHULZ. *Z. anorg. allgem. Chem.* 144, 225-47(1925), cf. C. A. 17, 2681.—Prepns. of  $Ta_2O_5$  hydrate at  $0^\circ$  and at  $100^\circ$  were made by dissolving  $7Na_2O \cdot 5Ta_2O_5 \cdot 40H_2O$  in 100 times its wt. of cold water and then adding slightly more than the calcd. amt. of 1 *N*  $HNO_3$  dropwise with stirring. The voluminous, amorphous ppts. ( $S_0$  and  $S_{100}$ ) were removed by a membrane filter and thoroughly washed with large amts. of water and

dried to const. wt. in vacuum over  $\text{H}_2\text{SO}_4$ . Dehydration and rehydration data were obtained and curves plotted. Neither  $\text{S}_{100}$  nor  $\text{S}_{100}$  gave indications of definite hydrates. Both showed characteristic hysteresis fields, that of  $\text{S}_{100}$  smaller and with lower content of water. Optical phenomena were not observed, both preps. remained white and chalky throughout the study. By adding 4 g  $\text{Ta}_2\text{O}_5$  in small portions to 12 g fused KOH, dissolving in 50–75 cc. water, letting stand 12–24 hrs for Ag to settle out, then concg. in vacuum over  $\text{P}_2\text{O}_5$  or by boiling, hexagonal prisms of  $7\text{K}_2\text{O} \cdot 5\text{Ta}_2\text{O}_5 \cdot 24\text{H}_2\text{O}$  were obtained which were easily and largely sol in cold water. From solns of this salt the less sol.  $7\text{Na}_2\text{O} \cdot 5\text{Ta}_2\text{O}_5 \cdot 22\text{H}_2\text{O}$ , needles, formed at  $100^\circ$ ,  $7\text{Na}_2\text{O} \cdot 5\text{Ta}_2\text{O}_5 \cdot 40\text{H}_2\text{O}$ , hexagonal, formed at room temp., and  $7\text{Li}_2\text{O} \cdot 5\text{Ta}_2\text{O}_5 \cdot 40\text{H}_2\text{O}$ , hexagonal, were prepd. by adding NaOH or LiOH. They might be considered salts of  $\text{H}_2[\text{Ta}(\text{TaO}_4)_2]$ . Cryoscopic mol. wt. detns. were excluded as no solvent other than water could be found. Diffusion researches were made with the K salt and with  $\text{Na}_4[\text{I}(\text{MoO}_4)_6]$  as control, following closely the method of Öholm (*Z. physik. Chem.* 50, 312(1904)). These indicated a mol. wt. of about 1750 for the tantalate and 1250 for the molybdoperiodate where 1450 and 1200 was to be expected. A 0.1 N soln. of the K salt had about the OH- ion concn. of 0.01 N KOH. Some studies on the cond. of solns. of the salts were made but results were inconst. and no definite conclusions could be drawn. A. R. M.

**Secondary valence of the hydroxyl group.** IV. **Aquo and pyridino tripyrocatechol-arsenic and antimonie acids.** H. REHLEN, A. SAPPER and G. A. KALL. *Z. anorg. allgem. Chem.* 144, 218–24(1925); cf. C. A. 17, 500, 18, 1406. —The prepn. of the following new salts is described ( $\text{A} = \text{C}_6\text{H}_4\text{O}_2$ ):  $\text{Na}[\text{PySbA}_3] \cdot 3\text{H}_2\text{O}$ , by rubbing up  $\text{H}[\text{SbA}_3] \cdot 2\text{Py}$  with a small excess of 2–4 N NaOH, centrifuging and drying on porous plate. It effloresces readily but loses no pyridine and may contain 6 instead of 3  $\text{H}_2\text{O}$ . Similarly the K salt +  $2\text{H}_2\text{O}$ ; it effloresces less readily than the Na salt. Excess of KOH did not displace the second pyridine.  $\text{Na}[\text{PyAsA}_3] \cdot 6\text{H}_2\text{O}$  by rubbing up  $\text{H}_2[\text{OAsA}_2] \cdot 2\text{Py}$  with the calcd. quantity of 2 N NaOH, sucking off and drying 12 hrs. over  $\text{H}_2\text{SO}_4$  at atm. pressure. Since only one Py is displaced in both acids, the other is in the complex and replaces  $\text{H}_2\text{O}$  formed by migration of H atoms in accordance with the principle previously demonstrated by R. that phenolic OH does not simultaneously have ionogenic and secondary valence. Contrary to Weinland these acids are invariably monobasic and the coordination no. of the As and Sb is 6. They should be formulated



salts of tribasic acids, are considered to be penetration compds. and are formulated  $[\text{Hg}_2\text{O} \cdot \text{AsA}_3]\text{H}$  and  $[\text{Hg}_2\text{O} \cdot \text{SbA}_3]\text{Hg}$ . This formulation makes clear why  $\text{H}_2\text{PO}_4$ , which rarely, possibly never, forms complexes in which the coordination no. of P is 6, forms no compds. with pyrocatechol. A. R. M.

**The potassium chlororuthenates and the coordination number of ruthenium.** S. H. C. BRIGGS. *J. Chem. Soc.* 127, 1042–8(1925). —Two salts of the formula  $\text{K}_2\text{RuCl}_3\text{H}_2\text{O}$  were obtained by Miotli (*Gazz. chim. ital.* 30, 511(1900)) and by Howe (*J. Am. Chem. Soc.* 23, 775(1901)). M.'s salt is clear yellow in dil. soln. and not affected by  $\text{Cl}_2$  or  $\text{Br}_2$ . H.'s salt is pink in dil. soln. and gives intense black solns. with  $\text{Cl}_2$  or  $\text{Br}_2$ . In both the water is not completely given off at  $200^\circ$  and must be in the complex. As the coordination theory does not admit isomeric forms, a restudy was undertaken. M.'s salts are prepd. by adding KCl to a cold acidified soln. of  $\text{RuCl}_3$ . The pptd. compd. is usually not homogeneous but becomes so after recrystn. from warm acidified water. A product agreeing closely with the formula was obtained direct when 8 g. KCl in 30 cc. water was added to a cold soln. of 5.63 g.  $\text{RuCl}_3$  in 130 cc. of soln. contg. sufficient HCl so that it fumed when heated on the water bath. When 2.7 g. KCl in 8.5 cc. of water was added to a cold soln. of 2 g.  $\text{RuCl}_3$  in 40 cc. HCl (d. 1.1), which had been kept 2 days, the ppt. corresponded to  $2\text{K}_2\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ . The same salt was obtained by passing  $\text{Cl}_2$  for 1.5 hrs. through a cold soln. of 1.5 g. of Howe's  $2\text{K}_2\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  and evapg. to dryness in vacuum over KOH and  $\text{H}_2\text{SO}_4$ . The residue of red-brown crystals and green-black scales was dissolved in HCl and evapd. in vacuum to crystn. when only the red-brown crystals formed. Their very dil. aq. soln. was yellow and gave no black color with  $\text{Br}_2$  or  $\text{Cl}_2$ . H.'s  $2\text{K}_2\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  is not blackened by  $\text{Br}_2$  or  $\text{Cl}_2$  in presence of very much acid. This was the only salt obtained pure in H.'s series. It is most conveniently prepd. by boiling 20 min. under reflux 450 cc. water contg. 7 cc. concd. HCl with 450 cc. EtOH, 2.8 g.  $\text{RuCl}_3$  and 2 g. KCl, distg. off the EtOH, letting stand a week and then evapg. to crystn. on the water bath. Before standing the soln. contains two or more salts, some evidence being obtained for  $\text{K}_2\text{RuCl}_3 \cdot 2\text{H}_2\text{O}$  and for  $\text{K}_2\text{RuCl}_3 \cdot 1\text{H}_2\text{O}$ .

A salt of the formula  $K_2RuCl_6 \cdot K_2RuCl_6OH$ , black, *cryst.*, was formed when air was bubbled for several days at water-bath temp. through an aq. soln. of H.'s  $2K_2RuCl_6 \cdot 3H_2O$ , which was kept strongly acid with HCl.  $RuO_3$  obtained by bubbling  $Cl_2$  through hot  $Na_2RuO_4$  soln. in a retort is conveniently collected by means of an adapter dipping under water in a 2 neck Woulfe bottle, a delivery tube from the second neck taking the fumes into an absorption app. filled with aq. alc. KOH.  $RuO_3$  falls to the bottom of the bottle as a yellow solid, which dissolves completely after some hrs. and the soln. can then be reduced by pouring into aq. KOH soln. contg. some EtOH. Arguments in favor of the coordination no. 8, rather than 7, in these compds. are stated. A. R. M.

The direct formation of oxybromides of mercury. H. PÉLABON. *Compt. rend.* 180, 1500-1(1925), cf. C. A. 19, 1105.—Twenty cc. distd.  $H_2O$ ,  $n$  mols. red  $HgO$  and  $m$  mols.  $HgBr_2$  were shaken in sealed, ordinary Na glass tubes for a long time, equil. being reached in about 4 weeks. When  $m > n$  bright yellow  $HgO \cdot HgBr_2$  is obtained as an extremely fine powder, settling with difficulty; when  $m < n$  chestnut-colored  $4HgO \cdot HgBr_2$  is obtained. When  $n < 4m$  the soln. contains 0.00018 mol.  $HgBr_2$  per 10 cc., which is greater than the normal soly. of  $HgBr_2$  in water (0.000145), the difference being due to the glass having been attacked. In quartz tubes equil. is reached only after 4 months and the same two oxybromides are obtained as relatively large, smooth, easily settling particles. When there is a large excess of  $HgBr_2$  over  $HgO$  there are also formed large colorless crystals of a third oxybromide with low  $HgO$  content. A. P.-C.

New mercury-ammonia compounds. P. RAY AND P. C. BANDOPADHYAY. *Quart. J. Indian Chem. Soc.* 1, 235-46(1925).—Dropwise addn. of a soln. of  $HgCl_2$  satd. with  $HgI_2$  to a large excess of strong  $NH_3$  soln. gave an orange ppt. of  $6NH_3 \cdot Cl \cdot NH_2I \cdot 2H_2O$  (1). It was washed with  $NH_3$  water and EtOH in succession and dried in vacuum over  $H_2SO_4$ . The same compd. was formed at various temps. and with varied concns. of chloride iodide soln. and from excess of boiling  $NH_3$  soln. By addn. of dil.  $NH_3$  to excess of chloride-iodide soln.,  $NH_3$  addn. being stopped before the white ppt. became yellowish,  $4NH_3 \cdot HgCl \cdot NH_2I \cdot 2H_2O$  (2) was obtained. It was washed with EtOH and dried in vacuum over  $H_2SO_4$ . Similarly to (1) but using  $(NH_4)_2CO_3$  soln., white  $NH_3 \cdot HgCl \cdot H_2O \cdot 2NH_3$ . Water turned it yellow. Similarly to (2) but with  $(NH_4)_2CO_3$  white  $NH_3 \cdot Cl \cdot 2H_2O \cdot NH_3$  was pptd.;  $HgBrI$  gave only more or less pure  $NH_3 \cdot HgBr$ . Freshly prepd.  $NH_3 \cdot HgCl$  was treated with concd. KSCN soln. in the cold, then heated on a water bath 3 hrs. with const. stirring. Much  $NH_3$  was evolved and yellow  $NH_3 \cdot SCN$  was formed. Similarly with concd. soln. of  $K_2CrO_4$  and heating 12 hrs. greenish yellow  $(OH)(H_3N)(H_3N) \cdot CrO_4$  was formed. (Cf. Hensgen, *Rec. trav. chim.* 5, 187(1887).) By digesting freshly pptd.  $Hg_3(AsO_4)_2$  with  $NH_3$  white  $(HO)(H_3N)(H_3N) \cdot AsO_4$  was obtained. A. R. M.

Cobaltammino chromates and chromatocobalti amines. P. RAY AND P. V. SARKAR. *Quart. J. Indian Chem. Soc.* 1, 289-96(1925); cf. Briggs, C. A. 13, 2322.—The following salts were prepd. by action of  $H_2CrO_4$  on carbonate-tetrammino and -pentammino salts.  $[(NH_3)_4CoCrO_4] \cdot Cr_2O_7 \cdot H_2O$  from slow addn. of 2 g.  $CrO_3$  in 20 cc. water to 4 g.  $[(NH_3)_4CoCO_3] \cdot (NO_3)_2$  in 60 cc. water; recrystd. from water contg. a few drops of AcOH.  $[(NH_3)_4CoCrO_4] \cdot Cr_2O_7 \cdot H_2O$  from slow addn. of 2 g. carbonate nitrate in 40 cc. water to 5 g.  $CrO_3$  in 20 cc. water and letting stand overnight; blackish *cryst.*, recrystd. from water; contg. a little  $CrO_4$ .  $[(NH_3)_4CoCrO_4] \cdot CrO_4 \cdot 1.5H_2O$ , red, *cryst.* by slow addn. of 2 g.  $CrO_3$  in 10 cc. water to 4 g. carbonatepentammino salt in 120 cc. water and recrystd. from hot water. By action of excess of  $H_2CrO_4$  brick red  $[(NH_3)_4Co \cdot H_2O] \cdot (Cr_2O_7) \cdot 2H_2O$  was obtained. Freshly pptd.  $Co(OH)_2$  from 25 g. nitrate was treated with 20 g.  $(NH_4)_2Cr_2O_7$  and 250 cc. concd.  $NH_3$  and a rapid current of air passed through 3-4 hrs. A red brown *cryst. powder* of  $[(NH_3)_4CoCrO_4] \cdot CrO_4 \cdot 2H_2O$  sep'd next day. Recrystn. from dil. AcOH gave  $[(NH_3)_4CoH_2O] \cdot CrO_4 \cdot (Cr_2O_7) \cdot H_2O$ . A. R. M.

The preparation of pure zirconium salts from zirconium earth by means of phosphate. J. H. DE BOER. *Z. anorg. allgem. Chem.* 144, 190-6(1925).—The 2 impurities most difficult to remove are Ti and Fe. Since many earths can be found which contain only a trace or no Ti, de B. devotes his attention to Fe. Zr can be sep'd from Fe in large quantities by use of the double fluoride with K and  $NH_4$ , the oxychloride, basic and acid sulfate, phosphate and finally by a method based upon hydrolytic dissociation. Of these methods, that in which the phosphate is pptd. is the most satisfactory. The Zr earth is fused with bisulfate; this is dissolved in  $H_2O$  and filtered, and the mixed hydroxides are pptd. with NaOH. They are washed by decantation and dissolved in concd. HCl, in considerable excess. Zr is then pptd. with  $H_3PO_4$ , washed well with HCl to remove Fe completely, then with  $H_2O$ , and the phosphate is then dissolved in HF or KF, from which it is again pptd. with NaOH in a pure condition. The hydroxide is used in the prepn. of other compds. The phosphate pptd. is very probably the orthophosphate, rather than

the pyrophosphate as some workers have believed. In the presence of strong acid the tendency is toward the formation of ortho salt. Phosphate pptd. in acid soln. shows no tendency to hydrolyze, and is more easily sol. in HF than phosphate pptd. in neutral soln. Zr can be sepd. from HF by fractional crystn. of the soln of the phosphates in HF, or by crystn. from soln. in  $\text{NH}_4$  or K bifluorides. H. STOERTZ

Double nitrates of metals of the cerium group with copper and cadmium. G. CAROBBI. *Atti accad. Lincei* [v], 33, 322-6(1924), cf. C. A. 19, 2174.—The following new compounds are described:  $2\text{Nd}(\text{NO}_3)_2 \cdot 3\text{Cu}(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$ , lilac crystals,  $d^{25}_D$  2.248; of the same form and obtained in the same way as the corresponding Ce compd.:  $2\text{Pr}(\text{NO}_3)_3 \cdot 3\text{Cu}(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$ , min., green crystals, and  $2\text{Sm}(\text{NO}_3)_3 \cdot 3\text{Cu}(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$ , both of the same type as the preceding, were obtained similarly. The double nitrates of Cd with Ce, La, and Nd were prepd. by evap. the mixed solns. of the nitrates over  $\text{H}_2\text{SO}_4$  at reduced pressure, below  $12^\circ$ . The following were obtained:  $2\text{La}(\text{NO}_3)_3 \cdot 3\text{Cd}(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$ , colorless tablets like those of the Cu compds.,  $d^{25}_D$  2.226,  $2\text{Ce}(\text{NO}_3)_3 \cdot 3\text{Cd}(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$ ,  $d^{25}_D$  2.294,  $2\text{Nd}(\text{NO}_3)_3 \cdot 3\text{Cd}(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$ , min. rose-colored crystals of the same cryst. form as that of the La salt. Jantsch has observed a parallelism among the mol. vol. curves of the double salts obtained from elements of the Ce-group and certain members of the Mg series of isomorphous elements, this is now shown to be shared by the curves of the double nitrates of Cu and Cd with elements of the Ce group. When the double salts given by the elements of the Mg family with any other single metal are placed in order of decreasing mol. vols., the succession, which has always been observed previously, is, Cd, Mn, Fe, Cu, Co, Mg, Zn and Ni. The double salts given by the members of this family with any one metal of the Ce-group, however, fall into the following sequence: Cd, Mn, Mg, Co, Zn, Ni and Cu. The Cu double nitrates afford an excellent means of sepg. La from Pr. B. C. A.

Titanous chloride and nitric acid. M. COBLENS and J. K. BERNSTEIN. *J. Phys. Chem.* 29, 750-2(1925).—Although  $\text{SnCl}_2$  reduces  $\text{HNO}_3$  to  $\text{NH}_4\text{OH}$ ,  $\text{FeSO}_4$  (a weaker reducing agent) and titanous chloride (a stronger reducing agent) give NO only. It was found that (1) 1 drop of  $\text{FeSO}_4$  soln. in a  $\text{SnCl}_2$  soln. causes the evolution of NO when  $\text{HNO}_3$  is added; (2) titanous chloride reduces NO and  $\text{N}_2\text{O}$  to  $\text{NH}_3$ ; (3) NO is evolved and no  $\text{NH}_3$  is formed when a  $\text{NaNO}_2$  soln. is added drop by drop to an acid titanous chloride soln.; (4)  $\text{N}_2\text{O}$  is evolved and no  $\text{NH}_3$  is formed when Ag hyponitrite is added slowly to an acid titanous chloride soln.; (5) titanous chloride has a sp. decomposing effect on nitrous acid and hyponitrous acids; (6)  $\text{NH}_4\text{OH}$  is formed when a  $\text{NaNO}_2$  soln. is added drop by drop to an acid  $\text{SnCl}_2$  soln.; (7)  $\text{NH}_4\text{OH}$  is formed when Ag hyponitrite is added slowly to an acid  $\text{SnCl}_2$  soln.; and (8)  $\text{NH}_3$  has been shown qualitatively to be one of the reduction products when  $\text{HNO}_3$  reacts with an excess of Na hyposulfite. W. C. EBAUGH

Double sulfates of rare earth and alkali metals. I. Lanthanum and potassium. F. ZAMBONINI and G. CAROBBI. *Atti. accad. Lincei* [v], 33, 301-8(1924); cf. Barre, C. A. 5, 435.—The equil. between an aq. La sulfate soln. and solid  $\text{K}_2\text{SO}_4$  at  $25^\circ$  has been studied, and the results are represented graphically by plotting the values of  $\text{K}_2\text{SO}_4/\text{H}_2\text{O}$  in the liquid phase as abscissas against those of  $\text{La}_2(\text{SO}_4)_3/\text{K}_2\text{SO}_4$  in the solid phase. Interpreted according to the phase rule (cf. Miller and Kenrick, *J. Phys. Chem.* 7, 259-68(1903)), this diagram indicates the formation of the following new (microcryst.) double salts:  $2\text{La}_2(\text{SO}_4)_3 \cdot 3\text{K}_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$  (monoclinic);  $\text{La}_2(\text{SO}_4)_3 \cdot 4\text{K}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  (spherical);  $\text{La}_2(\text{SO}_4)_3 \cdot 4.5\text{K}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$  (globular);  $\text{La}_2(\text{SO}_4)_3 \cdot 5\text{K}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$  (globular). II. Neodymium and potassium. F. ZAMBONINI and V. CAGLIOTI. *Ibid.* 308-13.—An examn. of the system  $(\text{Nd})_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  (cf. above) shows that, at  $25^\circ$ , the following double salts are formed:  $\text{Nd}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ ;  $\text{Nd}_2(\text{SO}_4)_3 \cdot 3\text{K}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ ;  $\text{Nd}_2(\text{SO}_4)_3 \cdot 4\text{K}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ ;  $\text{Nd}_2(\text{SO}_4)_3 \cdot 4\text{K}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ ;  $\text{Nd}_2(\text{SO}_4)_3 \cdot 5\text{K}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ ;  $2\text{Nd}_2(\text{SO}_4)_3 \cdot 3\text{K}_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$  (microcryst.; rosettes of pink monoclinic tablets,  $d^{25}_D$  3.026). B. C. A.

Separation of gallium from aluminum and iron. R. FRICKE. *Z. anorg. allgem. Chem.* 144, 267-8(1925); cf. C. A. 19, 1543.—F. admits the difficulty of sepg. Ga from large amts. of Fe and Al by repeated pptns. with  $\text{NH}_3$  and promises further investigation. A. R. M.

Action of ammonium chloride vapor on metals and similarity of ammonium salts and hydroxonium salts as acids. K. A. HOFMANN, F. HARTMANN and K. NAGEL. *Ber.* 58B, 808-17(1925).—Comparative expts. are described with dry HCl and  $\text{NH}_4\text{Cl}$  which show that the same amt. of HCl in the form of dry  $\text{NH}_4\text{Cl}$  at  $250-350^\circ$ , is 100 times as active on Cu, 40 times as active on Ni and Ag, and at least 5 times as active on Fe as it is in the free state. The H set free was measured and proved practically free from N, thus excluding decompn. of  $\text{NH}_3$ . Primary formation of ammino metal chloride was proved for each case. With Cu the max. yield of H was that which should result if

only undissociated mols of  $\text{NH}_4\text{Cl}$  reacted. Expts. with aq. solns. in sealed tubes showed that at  $200^\circ$  Cu can displace H completely from concd. aq.  $\text{HCl}$  while at this temp. an about equimol. soln. of  $\text{NH}_4\text{Cl}$  is but slightly acted on. It might be supposed that the dissociation  $\text{NH}_4\text{Cl} = \text{NH}_3 + \text{HCl}$ , already detectable at  $37^\circ$ , might be much greater at  $200^\circ$  but the expt. proves this not so and that at this temp. the ionic equl. is mainly involved. Cu, therefore, does not discharge  $\text{NH}_4^+$  and the discharged  $\text{NH}_4$  give  $\text{NH}_3$  and H. This expt. provides an important confirmation of Hantzsch's hydroxonium theory since HCl is shown to be nearly indifferent to Cu at  $300-20^\circ$  but, when combined with water, to react vigorously with it at  $200^\circ$ . It becomes an acid only when combined with water as  $[\text{OH}_2]\text{Cl}$  or with  $\text{NH}_3$  as  $[\text{NH}_4]\text{Cl}$ . Conclusion: The expts. show that dry  $\text{NH}_4\text{Cl}$  reacts with metals entirely like aq.  $\text{HCl}$ ,  $\text{M} + [\text{NH}_4]\text{Cl} = [\text{NH}_4\text{M}]\text{Cl} + \text{H}$  and  $\text{M} + [\text{OH}_2]\text{Cl} = [\text{OH}_2\text{M}]\text{Cl} + \text{H}$ . The dry ammonium salt is, therefore, an ammonium acid and the concd. aq.  $\text{HCl}$  a hydroxonium acid. In consequence of the much greater stability of the ammonium than the hydroxonium complex its reaction with metals proceeds with measurable velocity only at higher temps. Hg and As displaced no H from  $\text{NH}_4\text{Cl}$ . This is ascribed to lack of solid surface to condense H and liberate  $\text{H}_2$  and to the inability of As to form stable amino complexes. A. R. M.

Bismuth pyrocatecholates. A. ROSENHEIM AND I. BARUTSCHISKY. *Ber.* 58B, 891-3(1925).—The prepn. of salts of the general formula  $\text{R} \left[ \text{C}_6\text{H}_3\text{O}_2\text{Bi} \right] \text{H}_2\text{C}_6\text{H}_3\text{O}_2$

is described. All are bright yellow, well crystd. and sol. in water. They are prepd. by gradual addn. of Bi hydroxide or carbonate to a boiling alk. soln. of pyrocatechol protected from oxidation by a stream of  $\text{N}_2$ . Other salts can be prepd. by double decomposition. The aq. solns. are relatively stable but darken slowly in air with deposition of Bi-contg. ppts. Many have pyrocatechol of crystn. as well as water. The following are described ( $\text{A} = \text{C}_6\text{H}_5\text{O}_2$ ):  $\text{NH}_4[\text{BiA}_2]\text{AH}$ ;  $\text{H}_2\text{O}$ ;  $\text{K}[\text{BiA}_2]\text{AH}$ ;  $\text{Na}[\text{BiA}_2]\text{H}_2\text{O}$ ;  $\text{Ba}[\text{BiA}_2] \cdot 2\text{H}_2\text{O}$ ;  $\text{C}_6\text{H}_5\text{N}[\text{BiA}_2]$ . Preliminary notice is given of prepn. of  $\text{NH}_4[\text{SbA}_2]$  and similar salts and of  $\text{H}[\text{AsA}_2] \cdot 4\text{H}_2\text{O}$ , a much stronger acid than  $\text{HAsO}_4$ . A. R. M.

The complex salts of antimony trichloride. I. The complex salts of antimony trichloride and potassium chloride. SABURO MIYAKE. *Mem. Coll. Eng. Kyushu Imp. Univ.* 3, 187-93(1925).—See C. A. 19, 432. FOSTER DEN SNELL

A solid antimony hydride. E. J. WEEKS AND J. G. F. DRUCE. *J. Chem. Soc.* 127, 1009-72(1925).— $\text{Sb}_2\text{H}_4$ , analogous to Janovsky's  $\text{As}_2\text{H}_4$  (*Ber.* 6, 218(1874)), was obtained by electrolysis of  $\text{NaOH}$  soln. with Sb cathode, by passing  $\text{SbH}_3$  mixed with excess of  $\text{H}_2$  through solns. of  $\text{NaOH}$  more concd. than 5 N, by passing  $\text{SbH}_3$  over solid  $\text{NaOH}$ , and in the  $\text{SbH}_3$  generator when  $\text{SbCl}_3$  in concd.  $\text{HCl}$  dild. with an equal vol. of water was dropped into a flask contg. Zn and  $\text{HCl}$ . 0.6566 g. gave 29 cc.  $\text{H}_2$  on heating in vacuum; 0.4720 g. gave 0.0357 g.  $\text{H}_2\text{O}$ . It dissolves in fairly strong  $\text{HNO}_3$  but is insol. in other dild. acids and in concd.  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$ . It dissolves best in dild. aqua regia.  $\text{Sb}_2\text{H}_4$  reacted vigorously with fused  $\text{KNO}_3$ , while powdered reduced Sb showed no action; the residue after heating in vacuum behaved the same as the Sb. Dilatometric expts. in which  $\text{Sb}_2\text{H}_4$  was heated in xylene from  $15^\circ$  to  $112^\circ$  showed no transition pt. at  $101^\circ$  or any other temp. A. R. M.

Mechanism of the formation of malachite from basic copper carbonate. J. R. I. HERBURN. *J. Chem. Soc.* 127, 1007-13(1925).—By direct microscopic observation the course of the changes in transformation of the unstable amorphous  $5\text{CuO} \cdot 2\text{CO}_2$  into stable cryst. malachite,  $2\text{CuO} \cdot \text{CO}_2$ , was followed through a wide range of concns. both at room temp. and at  $100^\circ$ . In the cold transformation appears to be brought about through the intermediate agency of an aq. soln. of  $\text{CO}_2$  or of  $\text{NaHCO}_3$ . In presence of the former the resulting malachite consists of normal crystals, in presence of the latter entirely of spherocrystals probably produced through growth in a colloidal medium. At  $100^\circ$  thermal decompn. of the blue solns. prepd. by dissolving  $5\text{CuO} \cdot 2\text{CO}_2$  in satd.  $\text{NaHCO}_3$  soln. gives a surface film of interpenetrating spherocrystals which is disrupted into individual spherocrystals by further boiling. The cause of the change is attributed to loss of  $\text{CO}_2$  from the  $\text{NaHCO}_3$  with formation of stable  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$  and malachite. Presence of gelatin considerably retards the changes at both temps but does not affect their character or the products. This is believed to be one of the first cases recorded in which spherocrystals form the sole product of a normal chemical reaction. By 2 independent methods the mean diameter of the spherocrystals was found to be 6. Their density was found to be: by sp. gr. 3.64, by rate of fall 3.6 and by rate of transit across the microscopic field 3.7. The d. of natural malachite is 3.7-4.0. They were optically biaxial, like natural malachite, and clearly not amorphous substances under strain. A. R. M.

**Hydrates of calcium carbonate.** JOHN HUME. *J. Chem. Soc.* 127, 1036-4. The crystals were prep'd. in and kept in contact with 20% sucrose soln. In the hexahydrate exists below 10.4° and a pentahydrate below 17.0°. From su solns. crystals of hexahydrate form at temps. up to 17°, confirming Mackenzie (18, 27), because between 10.4° and 25° the metastable hexahydrate is first ppt'd and changes slowly to the form stable at the temp. of the expt. The hexahydrate in contact with water at or above 0° changes slowly into anhyd.  $\text{CaCO}_3$ . All dilatometric expts. showed a break in the vol.-temp. curve at 25° and there were signs of a transition at about 17° but attempts to isolate a hydrate lower than the pentahydrate were unsuccessful. The  $d_{15}$  of the hexahydrate was found to be 1.780. A. R. M.

**Constitution of polythionic acids.** F. RASCHIG. *Schwefel- u. Stickstoffstudien* 1924, 305-10.—The following structural formulas are proposed for Na tetra-,



tri-,  $\text{NaO} \begin{array}{c} \text{S} \\ \parallel \\ \text{SO}_2 \end{array} \text{SO}_2 \text{Na}$ , and penta-thionate,  $\text{NaO} \begin{array}{c} \text{S} \text{ S S} \\ \parallel \quad \parallel \\ \text{SO}_2 \text{SO}_2 \text{ONa} \end{array}$ , and dithionic acid,  $\text{HO} \text{SO}_2 \text{SO}_2 \text{OH}$ . B. C. A.

**Dithiomolybdates.** HUBERT TER MEULEN. *Chem. Weekblad* 22, 218-20 (1925).—On boiling with dil. HCl in a  $\text{H}_2$  stream  $(\text{NH}_4)_2\text{MoO}_7$ , prep'd. according to Krüss, decomposes, giving a mixt. of 2 parts insol.  $\text{MoS}_2$ , some of it forming a colloidal soln., and of 1 part molybdate, no  $\text{H}_2\text{S}$  is evolved. If  $\text{AcOH}$  is used instead of HCl all the  $\text{MoS}_2$  forms a very stable colloidal soln.  $\text{MoO}_3\text{S}$  was prep'd. as a brown-black ppt. from abs. alc. solns. of equiv. parts  $\text{MoO}_3\text{Cl}_3$  and  $\text{NaHS}$ . B. J. C. VAN DER HOEVEN

**Reduction of azoimide.** F. RASCHIG. *Schwefel- u. Stickstoffstudien* 1924, 213-20.—Acid reducing agents such as  $\text{SnCl}_2$  and  $\text{HI}$  reduce azoimide to  $\text{NH}_3$  and  $\text{N}$ . The reaction of azoimide with  $\text{NaHSO}_2$  may be represented thus:  $\text{NaHSO}_2 + \text{NaN}_2 + \text{H}_2\text{O} = \text{NH}_3 + \text{SO}_2\text{Na} + \text{N}_2 + \text{NaOH}$ , together with a subsidiary reaction:  $2\text{NaHSO}_2 + \text{NaN}_2 + \text{H}_2\text{O} = \text{Na}_2\text{S}_2\text{O}_3 + \text{NH}_3 + \text{NaOH}$ . In the reduction of azoimide by  $\text{Al}$  in alk. soln., hydrazine and  $\text{NH}_3$  are formed: (i)  $\text{N}_2\text{H} + \text{H}_2 = \text{N}_2 + \text{NH}_3$ ; (ii)  $\text{N}_2\text{H} + 3\text{H}_2 = \text{NH}_2 + \text{N}_2\text{H}_4$ . B. C. A.

**Oxidation of azoimide.** F. RASCHIG. *Schwefel- u. Stickstoffstudien* 1924, 201-12; cf. C. A. 10, 864.—Azoimide is unattacked by  $\text{KMnO}_4$  in neutral or alk. soln. In  $\text{H}_2\text{SO}_4$  soln., a slow oxidation takes place.  $\text{HN} = \text{O} = \text{N}_2\text{OH}$ . In addn., a portion of the azoimide appears to be oxidized to triatomic  $\text{N}$ , which then decomposes, yielding ordinary  $\text{N}$  mofs.  $\text{H}$  hypoazide,  $\text{N}_2\text{OH}$ , resembles  $\text{HClO}$  in its properties. It decomposes, yielding  $\text{O}$  and, probably, azoimide. By oxidation of azoimide in  $\text{H}_2\text{SO}_4$  or boric acid soln. in the presence of  $\text{Na}$  nitride,  $\text{HNO}_3$  is produced, the first stage being the

compd.  $\begin{array}{c} \text{N} \\ \parallel \\ \text{N} \end{array} \text{N} \begin{array}{c} \text{OH} \\ \parallel \\ \text{O} \end{array}$ , which then takes up more  $\text{O}$ , yielding the compd.,  $\begin{array}{c} \text{N} \\ \parallel \\ \text{N} \end{array} \text{N}(\text{OH}) \begin{array}{c} \text{O} \\ \parallel \\ \text{O} \end{array}$ , which by loss of  $\text{N}$  yields  $\text{HNO}_3$ . B. C. A.

**Oxidation of hydroxylamine.** F. RASCHIG. *Schwefel- u. Stickstoffstudien* 1924, 163-87.—When  $\text{NH}_2\text{OH}$  is oxidized by adding it together with dil.  $\text{H}_2\text{SO}_4$  to  $\text{KMnO}_4$  soln., the successive stages of oxidation are dihydroxyhydrazine,  $\text{OH}.\text{HN}.\text{NH}.\text{OH}$ ; dihydroxydihydrazine,  $\text{OH}.\text{N}.\text{N}.\text{OH}$ ; nitric oxide,  $\text{O}.\text{N}.\text{N}.\text{O}$ ; and a  $\text{N}$  tetroxide having the

constitution  $\begin{array}{c} \text{O} \quad \text{O} \\ \diagdown \quad \diagup \\ \text{N} \end{array} \text{N} \begin{array}{c} \text{O} \\ \parallel \\ \text{O} \end{array}$ , called by R.  $\sigma$ - $\text{N}$  tetroxide. The last compd. yields  $\text{HNO}_3$

and  $\text{N}$ :  $5\text{N}_2\text{O}_4 + 4\text{H}_2\text{O} = 8\text{HNO}_3 + \text{N}_2$ . Some  $\text{N}_2\text{O}$  is also formed. Complete oxidation to  $\text{HNO}_3$  cannot be effected with  $\text{KMnO}_4$ .  $\text{HClO}$  can oxidize  $\text{NH}_2\text{OH}$  completely to  $\text{HNO}_3$ . The oxidation of  $\text{NH}_2\text{OH}$  by  $\text{I}$  and other oxidizing agents is also discussed. The views of Kurtenacker and Neusser (C. A. 18, 796) are criticised. B. C. A.

**Action of sulfite, hydrogen sulfite, and sulfurous acid on hydroxylamine.** F. RASCHIG. *Schwefel- u. Stickstoffstudien* 1924, 225-40.—R. regards the reaction,  $\text{NH}_2.\text{OH}.\text{HCl} + \text{H}.\text{SO}_2.\text{ONa} = \text{NH}_2.\text{SO}_2.\text{ONa} + \text{H}_2\text{O} + \text{HCl}$ , as proof of the asymmetrical constitution of  $\text{NaHSO}_3$ . In the presence of  $\text{H}_2\text{SO}_4$ , the reaction with  $\text{NH}_2\text{OH}$  gives, besides aminosulfonic acid, a considerable amt. of  $(\text{NH}_4)_2\text{SO}_5$ , and  $\text{N}$  is evolved. It is assumed that the  $\text{H}_2\text{SO}_3$  is mainly present in the tautomeric form,  $\text{H}_2.\text{SO}_2.\text{O}$ , which by replacement of the  $\text{H}$  atoms may yield the diamide of a persulfuric acid,  $(\text{NH}_4)_2\text{SO}_5.\text{O}$ , and this oxidizes a further 2 mols. of  $\text{NH}_2\text{OH}$ , yielding  $\text{N}$  and sulfamide,  $(\text{NH}_4)_2\text{SO}_2.\text{O} + 2\text{NH}_2.\text{OH} = (\text{NH}_4)_2\text{SO}_2 + \text{N}_2 + 3\text{H}_2\text{O}$ ; the latter substance in aq. soln. decomposes into  $\text{NH}_3$  and aminosulfonic acid. It is calcd. that in aq. soln.  $1/2$  of the  $\text{H}_2\text{SO}_3$  is present in the normal asymmetric form and  $1/2$  in the tautomeric form. The difference in consti-

tution between H sulfites and monosulfites is also shown in the reaction with chloroamide, which in the former case yields Na chlorosulfonate, while in the latter case aminosulfonic acid is formed. (Cl, also Schaler and Köhler, *C. A.* 14, 156) B. C. A.

Combustion of ammonia to hydrazine and diimide. F. RASCHIG. *Schweefel- u. Stickstoffstudien* 1924, 221-4—The primary reaction in the combustion of  $\text{NH}_3$  in O is:  $2\text{NH}_3 + \text{O}_2 = \text{N}_2\text{H}_4 + 2\text{H}_2\text{O}$ , the diimide at once decomposing into its elements. A small part of the  $\text{NH}_3$  is oxidized to hydrazine, which can be detected with  $\text{BzH}$ . B. C. A.

The constitution of nitric acid and the nitronium salts formed with perchloric and sulfuric acids. A. HANTZSCH. *Ber.* 58B, 941-61 (1925).—The identity of the absorption spectrum of dil  $\text{HNO}_3$  with that of  $\text{KNO}_3$  soln. indicates a true acid form  $(\text{NO}_2)_2\text{H}$ , or better  $(\text{NO}_2)(\text{H}_2\text{O})$ , a hydronium salt being formed; while the analogy of absorption spectra of pure  $\text{HNO}_3$  and its solns in  $\text{Et}_2\text{O}$  to those of esters,  $\text{NO}_2\text{OR}$ , suggests the pseudo acid form,  $\text{NO}_2\text{OH}$ , in such media. The fairly high cond. of pure  $\text{HNO}_3$  is probably not due to ionization of  $\text{H}^+$  and  $\text{NO}_3^-$ , but to formation of "nitronium nitrate"  $[\text{NO}(\text{OH})_2][\text{NO}_2]$  or  $[\text{N}(\text{OH})_2][\text{NO}_2]$ , part of the  $\text{HNO}_3$  acting as a base. Evidence for similar compds with  $\text{H}_2\text{SO}_4$ , viz  $[\text{NO}(\text{OH})_2][\text{SO}_3\text{H}]$  and  $[\text{N}(\text{OH})_2][\text{SO}_3\text{H}]$ , in mixed acids was found by absorption spectra of such mixts. Weber [*Z. Chem.* 3, 366 (1871)] had isolated a compd corresponding to nitronium pyrosulfate  $[\text{NO}(\text{OH})_2][\text{S}_2\text{O}_7\text{H}]$ . The absorption spectrum of a soln. of  $\text{N}_2\text{O}_5$  in  $\text{H}_2\text{SO}_4$  was quite different. Nitronium mono- and diperchlorates were pptd. when the anhyd acids were mixed. They are stable non-explosive compds. By analogy, concd.  $\text{H}_2\text{SO}_4$  was considered to contain "sulfuryl-hum sulfate,"  $[\text{S}(\text{OH})_2][\text{SO}_3\text{H}]$ . Cond. of mixts. of these strong acids are consistent with these views. The various equilibria are discussed. A. W. FRANCIS

Preparation and properties of sulfur fluoride. II. M. TZENTNERSHVER AND C. STRENG. *Ber.* 58B, 914-8 (1925), cf. *C. A.* 18, 206—Details are given of the prepn. in vacuum according to  $\text{Ag}_2\text{F}_2 + 3\text{S} = \text{Ag}_2\text{S} + \text{S}_2\text{F}_6$  and a sketch of the app. is included.  $\text{S}_2\text{F}_6$  is heavy, colorless, forms dense clouds in air and in odor resembles  $\text{S}_2\text{Cl}_2$ . KOH causes instant sepn. of S which mostly redissolves giving a clear soln. When the gas is led into a dry flask, a deposit, usually yellow but sometimes colorless, settles out; this is completed after 12-24 hrs. and if the gas is then brought into another dry flask no further deposition takes place and this purified gas can be stored over Hg.  $\text{S}_2\text{F}_6$  from  $\text{Hg}_2\text{F}_2$  and S requires a high temp. for formation and a retort of Cu instead of glass must be used. This product gave a mol. wt. of 86 while that from  $\text{Ag}_2\text{F}_2$  gave 92-8. Strong heating of this latter product gave a gas of mol. wt. 88.2 so that decompn. at high temp. is certain.  $\text{S}_2\text{F}_6$  was found to vulcanize rubber readily. It paralyzes the respiratory organs and 1 vol. % killed mice in 10-15 min. With a fraction that was of doubtful homogeneity was found m p  $-105.5^\circ$ , b p  $-99^\circ$ ; liquid d. 1.5 at  $-100^\circ$ . A higher boiling fraction was certainly present. Fractionation studies will be made. A. R. M.

Nature of the halogen hydrides. A. HANTZSCH. *Ber.* 58B, 612-41 (1925); cf. *C. A.* 17, 2983, Halban, 19, 1642—Extensive exptl. evidence of H's theories regarding the nature of acids is arranged under the following heads: (1) b. p. regularities of the halogen hydrides and alkyl halides; (2) optical behavior of these 2 series and of  $\text{HSCN}$  and their alk. salts; (3) action of HCl, HBr and HI in concd. aq. soln. and in non ionizing media (a) on the velocity of inversion of cane sugar, (b) on indicators, (c) on the velocity of decompn. of diazoacetic ester, (4) true and pseudo oxonium halide salts and their chem. significance; (5) acidity of the halogen hydrides. If the abs. b. ps. of the alkyl halides,  $\text{C}_n\text{H}_{2n+1}\text{X}$ , be plotted with temps. as ordinate and the value of  $n$  as abscissa, nearly straight lines are obtained and the b. p. of the corresponding hydride,  $\text{HX}$ , lies on the prolongation of the line, not at  $n = 0$  but at  $n = -1$ . The great effect of association on b. p. is seen in HF for which the extrapolated value lies at  $149.2^\circ$ , observed for  $\text{H}_2\text{F}_2$ ,  $292.5^\circ$ . Similar regularities were found for  $\text{H}_2\text{S}$  and mercaptans and  $\text{PH}_3$  and alkyl phosphines. Agreement was less good for  $\text{NI}_3$  and  $\text{AsH}_3$ , indicating that they are somewhat associated. In aq.,  $\text{EtOH}$  and  $\text{Et}_2\text{O}$  soln. HBr was optically identical with  $\text{NH}_2\text{Br}$  and KBr and therefore is dissolved as hydroxonium bromide,  $\text{Br}[\text{H}_2\text{O}]$ ,  $\text{Br}[\text{H}_2\text{OC}_2\text{H}_5]$  and  $\text{Br}[\text{HO}(\text{C}_2\text{H}_5)_2]$ . On account of its instability HI could be studied only in aq. soln. and on account of its optical transparency HCl could not be used. The results of the 3 divisions of (3) above were concordant in indicating the order of strength to be  $\text{HIF} < \text{HCl} < \text{HBr} < \text{HI}$ . In non-aq. solns. HBr is much stronger than HCl and the acidity varies with the solvent used. In the indicator expts. using methyl orange the diln. was detd. at which the indicator salt through solvolysis changed into acid and indicator. HCl in water became inactive at 0.0005 N, in  $\text{Et}_2\text{O}$  at 0.02 N. HBr decomps. diazoacetic ester in aq. soln. with increasing concn. always much more rapidly than HCl; in non-ionizing solvents their activities are greater and more diver-

gent the more satd. the solvent, e. g.,  $\text{CHCl}_3$  and  $\text{C}_2\text{H}_2\text{Cl}_4$ , and are nearly independent of diln. In unsatd. solvents, e. g., toluene, the activities are much smaller and sink with increasing diln. Through the leveling action of water the great differences between  $\text{HBr}$  and  $\text{HCl}$  are reduced nearly to zero in consequence of the optically detected formation of hydroxonium halides,  $\text{X}[\text{H}_3\text{O}]$  or  $\text{X}[\text{H}(\text{OH})_n]$ . In  $\text{Et}_2\text{O}$ ,  $\text{HBr}$  and  $\text{HCl}$  behave very differently.  $\text{HBr}$ , present, according to the optical analysis as the salt  $\text{Br}[\text{HO}(\text{C}_2\text{H}_5)_2]$ , retains in this condition almost the same great activity as in  $\text{CHCl}_3$  and  $\text{C}_2\text{H}_2\text{Cl}_4$ , independent of diln.  $\text{HCl}$  in  $\text{Et}_2\text{O}$  becomes inactive toward both indicators and diazoacetic ester even at moderate diln., just as does  $\text{HNO}_3$ , apparently for the reason that it, also, is dissolved only as the etherate of the pseudo acid,  $\text{HCl} \cdot \text{O}(\text{C}_2\text{H}_5)_2$ . That the strength of the homopolar halogen hydrides increases in the same order as the reactivity of their alkyl compds is due to the same causes.  $\text{HF}$  with the greatest heat of formation has the least tendency to salt formation either by replacing  $\text{H}$  by metal or, by forming onium halides, to loosen the  $\text{H}$  binding and likewise holds the  $\text{C}$  most firmly in  $\text{FCH}_3$ , while in  $\text{HI}$  with its negative heat of formation the reverse is true.

A. R. M.

The preparation and properties of carbides. ERNST FRIEDERICH AND LIESELOTTE SRRIG. *Z. anorg. allgem. Chem.* 144, 169–89 (1925). — (1)  $\text{TiC}$ , made by heating  $\text{TiO}_2$  and  $\text{C}$  in an elec. furnace in an atm. of  $\text{H}_2$  at  $1700\text{--}1800^\circ$ , is a gray powder of metallic appearance, sol. in aqua regia, melts, as detd. by heating in a graphite furnace and measuring temp. with a Holborn-Kuribaum Pyrometer, about  $3430^\circ$  abs. Because of soot formation this probably is about  $100^\circ$  low. Sp. resistance at  $m. p.$  was 7.0 ohms, at room temp., 1.8–2.5 ohms. In detg. the  $m. p.$  of these carbides, the material is compressed into small bars. (2)  $\text{ZrC}$ , obtained by heating  $\text{ZrO}_2$  and  $\text{C}$  in  $\text{W}$  furnace at  $1900^\circ$  in atm. of  $\text{H}_2$ , is a gray powder, insol. in  $\text{HCl}$  or  $\text{HNO}_3$ , sol. in concd.  $\text{H}_2\text{SO}_4$ , d. 6.0, melts, as detd. by pyrometer on material heated in a furnace,  $3300^\circ$  abs. On account of the presence of much white vapor, this is probably about  $200^\circ$  low. The material produced contained 7–10% graphite, has a sp. resistance at room temp. of 0.7 ohm, and a hardness of 8–9. (3)  $\text{VC}$ , made by heating together  $\text{V}_2\text{O}_5$  and  $\text{C}$  at  $1100^\circ$  in  $\text{H}_2$ , is very hard and brittle,  $m. 2810^\circ$ , sp. resistance at  $2500^\circ$  3.2 ohms and at room temp. 1.5 ohms. (4)  $\text{TaC}$ , made from the oxide and  $\text{C}$  at  $1250^\circ$ , is dark gray when pure, burns brightly when ignited in air, d. 13.96, hardness after fusion 9–10,  $m.$  about  $4100^\circ$  abs. (higher than any other chem. compd.). Sp. resistance of the fused material is 3–5 ohms. The best results were obtained by measuring current flow and voltage drop between 2 points on the surface in an atm. of  $\text{N}_2$ . (5)  $\text{CbC}$ , from  $\text{Cb}_2\text{O}_3$  and  $\text{C}$  in  $\text{H}_2$  at  $1200^\circ$ , is a gray-violet powder, insol. in all acids, burns brilliantly on ignition, d. 7.56, hardness after fusion 9–10,  $m.$  about  $3650^\circ$  abs., sp. resistance at room temp. 1.47 ohms. (6)  $\text{Cr}_3\text{C}$ ,  $m.$  about  $2650^\circ$ , sp. resistance 1.6 ohm at room temp., is very hard, easily scratching corundum. (7)  $\text{Mo}_3\text{C}$ , from 2 parts  $\text{Mo}$  and 1 part  $\text{C}$  at  $1200^\circ$ ,  $m.$   $2580^\circ$  abs., sp. resistance 1.81 ohms at  $m. p.$  and 0.975 ohms at room temp. The  $m. p.$  of  $\text{Mo}_3\text{C}$  is lower than that of the metal. Its hardness is about 7. (8)  $\text{MoC}$ , from 1 part  $\text{Mo}$  and 1 part  $\text{C}$  at  $1500\text{--}1600^\circ$ ,  $m.$  at the same temp. as the metal, sp. resistance at  $m. p.$  0.7 ohm, at room temp. 0.49 ohm. (9)  $\text{WC}$ , from  $\text{W}$  and  $\text{C}$  at  $2000^\circ$  in  $\text{H}_2$ ,  $m.$   $3140^\circ$  abs. (lower than the metal), sp. resistance at  $m. p.$  2.6 ohms, at room temp. 0.53 ohms. (10)  $\text{SiC}$ , from  $\text{Si}$  and  $\text{C}$  at  $1600^\circ$ , gray-green powder, does not conduct current. (11)  $\text{Sc}_2\text{C}_3$  is a conductor. (12)  $\text{CaC}_2$  has sp. resistance at room temp. of about 6 million ohms.

H. S.

Double decompositions of siloxene with halogen compounds and their initiation by light and chemical reactions. H. KAUSKY AND H. THIELE. *Z. anorg. allgem. Chem.* 144, 197–217 (1925); cf. *C. A.* 18, 3012. — The  $\text{H}$  of siloxene can be replaced by halogen in double decompns. involving siloxene and hydrogen halides or org. halogen compds. such as halogen alkyls and aryls and halogen-substituted acetic acid. Gaseous  $\text{HBr}$  reacts quant. with siloxene either with or without the presence of light to produce monobromosiloxene,  $\text{Si}_4\text{O}_6\text{H}_8 + \text{HBr} = \text{Si}_4\text{O}_6\text{H}_7\text{Br} + \text{H}_2$ . This reaction is evidence for the presence of 6 atoms of  $\text{Si}$  in the siloxene mol. A similar reaction takes place between siloxene and organic halogen compds. in the presence of light.  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , or an amine reacts with the halogen-substituted siloxene to form hydroxysiloxene or aminosiloxene. Siloxene absorbs only light of short wave length, but the reaction between org. halogen and siloxene can be sensitized to long wave lengths by the addition of a very small quantity of hydroxysiloxene or a dye. Since colored products are formed as the reaction proceeds (the halogen, amino and hydroxy derivs. are colored) there is an autosensitization to light of long wave length. The reaction may be started in the dark by the energy produced during the oxidation of a very small part of the siloxene with oxygen. Siloxene produced in the nascent state from  $\text{CaSi}_2$  and  $\text{HCl}$  also contains enough energy to react with org. halogen compds. in the dark. There is

a close connection between the luminescent properties of siloxene and its derivs., and the photochemical and induced reactions described above.

R. J. H.

The explosion of ammonia with carbon monoxide and nitrogen. J. W. BEESON AND J. R. PARTINGTON. *J. Chem. Soc.* 127, 1146-50(1925); cf. Partington and Prince, *C. A.* 19, 400—Mixts. of  $\text{NH}_3$  with  $2\text{CO} + \text{O}_2$  in varying proportions were exploded at an initial temp. of  $85^\circ$  and pressure 380 mm. so that no steam condensed. Mixts. in which  $\text{NH}_3/(2\text{CO} + \text{O}_2) > 0.924$  could not be ignited by sparks. All mixts. that could be ignited showed approx. the same decompn. of  $\text{NH}_3$ , 95.3%. In some mixts. richer in  $\text{NH}_3$  than 40.5% a period of induction was observed. The results are, therefore, quite different from those obtained with electrolytic gas. A sketch of the app. is given.

A. R. M.

Preparation of pure hydrogen. V. RAYLE AND M. TAMELE. *Chem. Listy* 18, 389-90(1924)—Amalgamated Zn does not dissolve in dil. acids because of the high overvoltage of the H; contact with a Pt sheet, however, immediately induces a rapid evolution of H from the Pt. An app. is described and illustrated which allows a continuous supply of pure H under considerable pressure to be obtained by making use of this reaction.

B. C. A.

MELLOW, J. W. Modern Inorganic Chemistry. New York and London: Longmans Green & Co. 1103 pp. \$4.25. (12s. 6d. net.) Reviewed in *Chem. Trade J.* 76, 675(1925).

## 7—ANALYTICAL CHEMISTRY

WILLIAM T. HALL

The potentiometric standardization of potassium permanganate solutions with sodium oxalate. C. DEL FRESNO. *Z. Elektrochem.* 31, 189-200(1925)—The electrometric end point is obtained in titrating  $\text{Na}_2\text{C}_2\text{O}_4$  solns. with  $\text{KMnO}_4$  just before the soln. turns pink with a slight excess of  $\text{KMnO}_4$ . The results are accurate although more time is required than in the usual method. Also in *Anales españ. fis. quim.* 23, 231-41(1925).

W. T. H.

Use of iodic acid and potassium bicarbonate for the preparation of standard solutions. M. RUSZKOWSKI. *Roczniki farm.* 2, 108-9(1924).

B. C. A.

Electrometric titrations using quinhydrone. H. NIKLAS AND A. HOCK. *Z. angew. Chem.* 38, 407-9(1925).—Within the range  $p_H = 2.05-8.0$  the platinized Pt electrode and  $\text{H}_2$  generator can be discarded in electrometric titrations provided a little quinhydrone is added to the soln. This substance is hydrolyzed somewhat and sufficient  $\text{H}_2$  formed to maintain a partial pressure of  $10^{-24.4}$  atm. The results of several titrations show satisfactory agreement with results obtained with the usual  $\text{H}_2$  electrode or by indicator work. It was found advisable to titrate in a closed vessel and in contact with air free from  $\text{CO}_2$ . As comparison electrode, the usual calomel cell can be used or the *N* quinone electrode which is 0.01 *N* in  $\text{HCl}$  and 0.09 *N* in  $\text{KCl}$ . When the latter is used,  $p_H = 2.01 + (\pi/0.0577)$ , where  $\pi$  is the measured e. m. f.

W. T. HALL

Nessler's reagent without potassium iodide. L. W. WINKLER. *Z. Nahr. Genussm.* 49, 163-5(1925).—Dissolve 1.0 g.  $\text{HgI}_2$  with 5 g.  $\text{KBr}$  and 2.5 g.  $\text{NaOH}$  in 25 cc. natural  $\text{H}_2\text{O}$  (about  $10^\circ$  hardness); allow to stand overnight and remove the clear supernatant liquid. It will not cement glass stoppers to bottles. Prep. a Rochelle salt soln.: 100 g. crystals in 200 cc. warm  $\text{H}_2\text{O}$ , filter through cotton, add 1.0 g.  $\text{NaOH}$ , boil 10 min. to remove  $\text{NH}_3$  and make up to 250 cc. Add 0.2 g.  $\text{HgI}_2$  and shake. Use the supernatant liquid. This soln. will prevent a ppt. forming when Nessler's soln. is added to natural  $\text{H}_2\text{O}$ . To 10-cc. sample add 10 drops each of Nessler's and the Rochelle salt solns. A color indicates at least 0.1 mg.  $\text{NH}_3$  per l. The reagent is not suitable for quant. detns.

F. E. R.

Rapid electrolytic separations by means of graded potentials. A. LASSIEUA. *Ann. chim.* 3, 269-324(1924); cf. *C. A.* 19, 1833—In the last installment of this interesting monograph, the following topics are discussed. Pb, its sepn. from Bi, Sb and Cu; Sn, its sepn. from Sb and Pb. Most of the methods described are not new but L. describes the tests that he has made and gives much valuable information concerning the technic.

W. T. H.

Potentiometric hydrogen-ion measurement with non-gas electrodes. H. C. PARKER. *Ind. Eng. Chem.* 17, 737-40(1925)—Many metals and combinations of metal and oxide were tested to see if they could be used to replace the  $\text{H}_2$  electrode in poten-

tiometric measurements. Platinized  $\text{Au-Mn}_2\text{O}_3$  and platinized  $\text{Pt-Mn}_2\text{O}_3$  gave good results throughout a considerable range of  $p_{\text{H}}$ . A no. of similar electrodes, such as  $\text{W-Co}_2\text{O}_3$ ,  $\text{W-MnO}_2$  and  $\text{W}$  alone gave good values in alk. solns. The theory regarding such electrodes is discussed and 2 possible explanations are offered. These electrodes are particularly free from poisoning effects and require but little attention. Their use seems promising for the control of  $p_{\text{H}}$  in com. work. W. T. H.

Inexpensive method for determining lead. W. W. SCORR *Ind. Eng. Chem.* 17, 678-680 (1925).—Dissolve the  $\text{PbCrO}_4$  ppt. produced in the usual way, in  $\text{HCl}$  and  $\text{NaCl}$  mixt. and titrate the chromic acid with  $\text{FeSO}_4$  using diphenylamine as indicator. Not more than 10 cc. of 12  $N$   $\text{HCl}$  should be present in 150 cc. of soln. or the addn. of acetate is necessary to reduce the acidity. W. T. H.

Recommended specifications for analytical reagent chemicals. W. D. COLLINS, H. V. FARR, JOE ROBIN, G. C. SPENCER AND EDW. WICKERS. *Ind. Eng. Chem.* 17, 756-60 (1925).—Specifications are given for  $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{NH}_4\text{OH}$ ,  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ ,  $\text{NH}_4\text{CNS}$ ,  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{I}_2$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{KOH}$ ,  $\text{AgNO}_3$ ,  $\text{NaOH}$  and  $\text{Na}_2\text{C}_2\text{O}_4$ . W. T. H.

Separation of manganese in the analysis of limestone and similar materials. ALICE W. EPPERSON *Ind. Eng. Chem.* 17, 714-5 (1925).—To the filtrate from the  $\text{SiO}_2$  at a vol. of about 175 cc. and contg. 10-16 cc. of concd.  $\text{HCl}$ , add 5 drops of 1% rosolic acid in alc. and 1 g.  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ . Neutralize the cold soln. with  $\text{NH}_4\text{OH}$ , heat and boil 1 min. Filter and wash with hot 2%  $\text{NH}_4\text{Cl}$  soln. In the filtrate  $\text{Ca}$  and  $\text{Mg}$  can be detd. without fear of error due to  $\text{Mn}$ . W. T. H.

Explosion method for peroxide fusions. W. F. MUEHLBERG. *Ind. Eng. Chem.* 17, 690-1 (1925).—The method advocated consists in mixing the sample with sugar  $\text{C}$  and  $\text{Na}_2\text{CO}_3$  and igniting with the aid of a string while cooling the crucible with water. In the analysis of  $\text{Fe-Si}$  a slight residue can be filtered off after the subsequent leaching and the wt. deducted from the original wt. of sample. W. T. H.

The standardization of the industrial methods for the determination of zinc in minerals. RY. OLIVIER. *Bull. soc. chim. Belg.* 33, 543-9 (1924).—A historical discussion of the Schaffner method and its modifications (cf. Beyne, C. A. 18, 1620, 3571). WM. B. PLUMMER

Dry method of determining zinc contained in brass, bronze and other alloys. T. SHIBATA AND B. KAMIFUKU. *Mem. College Sci. Kyoto Imp. Univ.* 8, 167-77 (1925).—Weigh 0.5 g. of alloy and 0.5 g. of pure  $\text{Sn}$  into a small graphite crucible contg. some wood charcoal. Cover with more charcoal and heat at about  $220^\circ$  for 30-40 min. and then at  $980^\circ$  for 90 min. Cool and weigh. The loss in wt. represents the  $\text{Zn}$ . W. T. H.

Bromometric determination of thiocyanates and cyanides. F. OBERHAUSER. *Z. anorg. allgem. Chem.* 144, 257-62 (1925).—The reaction  $\text{CNS}^- + 4\text{Br}_2 + 4\text{H}_2\text{O} \rightarrow 7\text{Br}^- + \text{BrCN} + 8\text{H}^+ + \text{SO}_4^{--}$ , takes place slowly, especially toward the end. To det.  $\text{CNS}^-$  it is best to proceed thus. To the  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$  soln. add 0.1  $N$   $\text{Br-KBr}$  soln. until the soln. is distinctly yellow. Allow to stand 10 min. in a stoppered bottle, add an excess of standard arsenite soln., add indigo carmine and styphnic acid as indicators and titrate with  $\text{Br-KBr}$ . To det.  $\text{Cu}$ , ppt. as  $\text{CuCNS}$  in the usual way. Treat the washed ppt. together with the filter with  $\text{HCl}$  and  $\text{Br}$  exactly as in the analysis of thiocyanate. Cyanide reacts with  $\text{Br}$  as follows:  $\text{KCN} + \text{Br}_2 = \text{CNBr} + \text{KBr}$ . This reaction is also slow toward the end.  $\text{K}_3\text{Fe}(\text{CN})_6$  can be oxidized to ferricyanide by means of  $\text{Br}$  in  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$  soln. with indigo carmine and styphnic acid as indicator.  $\text{K}_3\text{Fe}(\text{CN})_6$  can be reduced to ferrocyanide by means of a slight excess of standard arsenite soln. and the excess titrated with  $\text{Br}$  as follows: To the soln. to be analyzed add an excess of 0.1  $N$  arsenite soln., 10 cc. of 2  $N$   $\text{ZnSO}_4$  soln. and enough  $\text{NaOH}$  to dissolve the ppt. that first forms. Heat to  $50^\circ$  until the soln. is colorless (15 min.). Cool, make acid with  $\text{HCl}$ , add indigo carmine and styphnic acid and titrate the excess arsenite with  $\text{Br}$  soln. Another method for analyzing ferro- or ferricyanide is based on the decompn. with  $\text{HgCl}_2$ :  $2\text{Fe}(\text{CN})_6^{--} + 8\text{HgCl}_2 + 3\text{Mg}(\text{OH})_2 = 6\text{Hg}(\text{CN})_2 + \text{Hg}_2\text{Cl}_2 + 2\text{Fe}(\text{OH})_3 + 3\text{Mg}^{++} + 14\text{Cl}^-$ . Take 0.4 g. of substance and heat to boiling with 20 cc. of 4  $N$   $\text{NaOH}$  and 20 cc. of 6  $N$   $\text{MgCl}_2$  soln. Boil 5 min., add 120 cc. of 0.1  $N$   $\text{HgCl}_2$  soln. and boil 30 min. Cool, add  $\text{H}_2\text{PO}_4$  or  $\text{HF}$  to decolorize  $\text{FeCl}_3$ , make acid with  $\text{H}_2\text{SO}_4$  and titrate for cyanide as described above. W. T. H.

Treatment of malaccon. Separation of hafnium and of zirconium. MILLE. M. MARQUIS, P. URBAIN AND G. URBAIN. *Compt. rend.* 180, 1377-80 (1925).—Malaccon is a silicate of  $\text{Zr}$  contg.  $\text{Hf}$ ,  $\text{Th}$ ,  $\text{Cb}$ ,  $\text{U}$  and  $\text{Ta}$ . Fusion with  $\text{K}_2\text{S}_2\text{O}_7$  attacks it best but treatment with concd.  $\text{H}_2\text{SO}_4$  is more economical. After the excess acid is boiled off, a concd. soln. of sulfates is obtained from which practically all of the  $\text{Zr}$  and  $\text{Hf}$  can be pptd. by means of  $\text{K}_2\text{SO}_4$ . The double sulfate of  $\text{Zr}$  is less sol. than that of  $\text{Hf}$  so that

it is possible to sep these 2 elements by fractional pptn. The double sulfate of Zr is more sol in satd  $\text{Na}_2\text{CO}_3$  than is the corresponding III compd. On the basis of these facts a good sepn can be obtained in about 20 treatments. W. T. H.

New iodometric methods which depend on the formation and measurement of iodine cyanide. IV. R. LANG, Z. anorg allgem Chem 144, 75-84(1925); cf. C. A. 19, 1830.—*Detn of bromide*—The reaction  $\text{Br}^- + \text{HCN} + 2\oplus \rightarrow \text{BrCN} + \text{H}^+$  can be used for the exact detn of  $\text{Br}^-$ . The measurement can be made on the basis of oxidizing soln required, or the excess of oxidizer may be removed and the  $\text{BrCN}$  titrated with thiosulfate after the addn. of KI. Reducing agents such as acid solns of arsenite, hydrazine, thiocyanate, oxalate, mirite and ferrous salt do not reduce  $\text{BrCN}$ ; so it is easy to remove the excess of oxidizer. (a) To a soln of 0.1-0.3 g KBr in 10-30 cc of water add 50 cc of 5 N  $\text{H}_2\text{SO}_4$ , 10 cc of 0.5 N KCN and an excess of standard  $\text{KIO}_3$ . Keep the mixt. at 42-48° for 2 hrs. Then, after cooling, add 15 cc. of 6 N HCl, a little starch and enough  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$  to react with the excess  $\text{KIO}_3$ . Finally add more  $\text{KIO}_3$  until the iodo starch reaction disappears. (b) To the  $\text{Br}^-$  soln add 5-10 cc of sirupy  $\text{H}_3\text{PO}_4$ , 5 cc 0.5 N KCN and 10-15 cc. of N  $\text{KMnO}_4$ . After 5 mins. discharge the  $\text{KMnO}_4$  color by carefully adding Mohr's salt. Then add 1 g. of KI, starch and titrate with  $\text{Na}_2\text{S}_2\text{O}_3$ . *Detn of iodide, bromide and chloride in the presence of one another.*—(a) Iodate Method. To det Br and I, treat the soln contg. not more than 0.3 g of either bromide or iodide, with 1-2 g NaCl, 50 cc of 5 N  $\text{H}_2\text{SO}_4$ , 10 cc of 0.5 N KCN and a little starch. Det iodide by direct titration with  $\text{KIO}_3$ . Then add an excess of  $\text{KIO}_3$  and det the Br as described above. (b) Thiosulfate method. To det. iodide, treat the soln of the halides with 5 cc of 0.5 N KCN and 5-10 cc. of AcOH. Add freshly pptd  $\text{MnO}_2$ , mix well and dissolve the unused ppt. by means of Mohr's salt. Add  $\text{H}_3\text{PO}_4$  and titrate with  $\text{Na}_2\text{S}_2\text{O}_3$ . To det the sum of the bromide and iodide, add 5-10 cc. of sirupy  $\text{H}_3\text{PO}_4$ , 10 cc. of 0.5 N KCN, some starch and 0.1 N  $\text{KMnO}_4$  to the disappearance of the starch blue. Then add 15 cc of N  $\text{KMnO}_4$  and decolorize after 15 min. with Mohr's salt. Add 2 drops of 0.1 N  $\text{KCNS}$ , 0.5 g of KBr, a little more starch. Titrate with  $\text{Na}_2\text{S}_2\text{O}_3$ , adding 1 g of KI toward the end. (c) To the soln. of the halides, add 10 cc of 6 N HCl, 10 cc. of 0.5 N KCN and a little starch. Titrate the iodide by adding  $\text{KIO}_3$  until the soln is colorless. Now add 5 g of  $\text{NH}_4\text{H}_2\text{PO}_4$ , 5 cc. of sirupy  $\text{H}_3\text{PO}_4$  and 15 cc. of N  $\text{KMnO}_4$ . Then titrate with  $\text{Na}_2\text{S}_2\text{O}_3$  which indicates all of the  $\text{BrCN}$  and 1.5 times the  $\text{ICN}$ . In all cases, det Cl by the Volhard argentometric titration, either getting the total halogen content in this way, or else carrying out the titration after the removal of the Br and I. W. T. H.

Detection of hydrocyanic acid in toxicology by means of the reaction of Chelle. G. MAGNIN J. pharm chim [8], 1, 336-9(1925).—The claim that HCN poisoning may be detected by Chelle's test (C. A. 13, 3107) 1 or 2 months afterwards is verified on 12 samples, 3 to 7 yrs old, of viscera kept in a medical museum. The direct method of detn., with  $\text{H}_2\text{PO}_4$  applied to the same samples, gave negative results. Control samples, 2 to 4 yrs old, gave negative results by either method. S. WALDBOTT

Is the phenolphthalein reaction a certain criterion of the carbonate content of bicarbonates? ANON. J. pharm. Belg 7, 361-3, 377-9(1925).—The method of the Belgian Pharm. III for the estn. of  $\text{Na}_2\text{CO}_3$  in  $\text{NaHCO}_3$  is an adaptation of the method of Warder for the detn of alkali carbonates in bicarbonates. It consists of adding 3 drops of phenolphthalein indicator to 1 g of bicarbonate dissolved in 20 cc. of  $\text{H}_2\text{O}$ , titrating with N HCl to decoloration, then adding methyl orange and titrating to a pink orange color. The Pharm requires that the amt. of N HCl needed for complete decoloration shall not exceed 0.2 cc. Theoretically this corresponds to 2.12% of  $\text{Na}_2\text{CO}_3$ . From the results obtained in the testing of a no. of pharmaceutical and c. p. samples of  $\text{NaHCO}_3$  by this method and by the method of Winkler, it is concluded that the requirements of the Belgian Pharm are unattainable. None of the samples tested satisfied this requirement. An exceptionally pure sample which assayed 99.13% of  $\text{NaHCO}_3$  and 0.42% of  $\text{Na}_2\text{CO}_3$  required 0.3 cc of N HCl for complete decoloration. A. G. DUKEZ

Rapid separation of sulfur precipitated in analytical reactions. MAX AWSCHATON. Anal. soc. quim. Argentina 12, 461-2(1921).—The milky S produced by the oxidation of  $\text{H}_2\text{S}$  in analytical reactions is pptd. as a coherent pellicle by a single vigorous shaking with ether. MARY JACOBSEN

Analysis of fluosilicate and fluoride mixtures in organic substances. O. NOETZEL. Z. Nahr. Genussm 49, 204-6(1925).—Since these salts differ in toxic properties it is important to distinguish between them. Fluosilicate can be detected by treating with  $\text{H}_2\text{SO}_4$  and collecting the  $\text{SiF}_4$  evolved on a slide bearing a drop of  $\text{H}_2\text{O}$  and examg microscopically. For the detection of F use the common etching test: Coat the

glass with a special heat-resisting lacquer prep'd by dissolving 6 g. benzoin in 10–15 cc. ether and mixing with 100 g. collodion; dry in an oven a few min. Evolve HF from a Pt dish by heating on a sand bath at 130–149° for  $1\frac{1}{2}$  hr. The lacquer is removed by scraping and by washing with alc. and ether. For the detn., mix the sample with  $\text{Na}_2\text{CO}_3$  sufficient to make it alk. and ignite in a Pt dish. Macerate the ash with  $\text{H}_2\text{O}$  contg. enough HCl to make it acid. Add  $\text{NH}_4\text{OH}$  and  $(\text{NH}_4)_2\text{CO}_3$  in excess and heat as long as  $\text{NH}_3$  is evolved. Make up to about 30 cc. and sat. with NaCl by adding salt and evap. until crystals begin to form. Add enough  $\text{H}_2\text{O}$  to bring crystals into soln. and boil a short time. Allow to stand a few min., filter, and wash with 10% NaCl. Ignite the paper in a Pt dish, add HCl and evap. 3 times; heat to 140°. Take up the residue with dil. HCl, filter, wash and ignite (as  $\text{SiO}_2$ ). Calc. %  $\text{Na}_2\text{SiF}_6$  and % F from this. Det. total F by the method previously described (C. A. 19, 1917).

FRANK E. RICE

**Destruction of organic matter by perhydrol:** its application in toxicology. G. MAGNIN. *J. pharm. chim.* [8], 1, 333–6 (1925).—To 50 g. of viscera in a 1-l. flask, add slowly 50–75 cc. of perhydrol, after 12 hrs. the org. matter is destroyed as if treated with Cl or Br. Warming, or addn. of NaOH, hastens the reaction. Treat the product with HCl until acid, filter and add  $\text{SO}_2$ . Expel the excess of  $\text{SO}_2$  by heat, then ppt. metals by a current of  $\text{H}_2\text{S}$  as usual. Addns. of 0.02% of Cu, Bi, Pb, Hg, Ba, Sb, Zn and Sn and of 0.01% of As were easily recovered.

S. WALDBOTT

**The law of reduction strength of organic compounds in alkaline solution and the determination of the sugars by means of graded analysis and by the separation of colloidal cuprous oxide.** H. RUOSS. *Biochem. Z.* 151, 337–56 (1924).—Fehling's soln. of a given Cu content reduced varying amts. of a sugar soln. depending upon the diln. of the titrated soln. as well as upon its alk. A volumetric method which involves only the use of a pipet in the detn., of sugar consists of the addn. of increasing amts. of a standard Fehling's soln. to aliquots of the unknown sugar soln. placed in successive tubes, and a detn. of the amt. which just leaves  $\text{Cu}^{++}$  in soln. The end point may be easily detected by means of  $\text{K}_4\text{Fe}(\text{CN})_6$ . If 100 cc. of an alk. metallic salt soln. or an alk. dye soln. be reduced by Z cc. of a soln. of an org. substance S, the latter soln. contains  $(A/Z + B + CZ)$  % of S. If the 100 cc. is brought to a normality  $n$  by dilg. with  $\text{H}_2\text{O}$ , it is reduced by  $(D + E/n + F/n)$  mg. of the substance S. A, B, C, D, E and F are const.

W. D. LANGLEY

**New method for detecting minute quantities of hexamethylenetetramine, formaldehyde and methanol.** F. CALZOLARI. *Scritti di scienze med. e nat.*, Ferrara 1923, 305; *Schweiz. Apoth. Ztg.* 63, 195 (1923).—To a 0.1 + % soln. of  $\text{C}_6\text{H}_{11}\text{N}_4$ , add equal vols. of a satd.  $\text{MgSO}_4$  soln. and a freshly satd. soln. of  $\text{K}_4\text{Fe}(\text{CN})_6$  to obtain a yellow, cryst. ppt. of  $\text{MgKFe}(\text{CN})_6 \cdot 2\text{C}_6\text{H}_{11}\text{N}_4 \cdot 12\text{H}_2\text{O}$ . The reaction is sensitive to 0.02 mg. of urotropine. To test for  $\text{CH}_3\text{O}$ , evap. 1 cc. of the soln. with 20%  $\text{NH}_4\text{OH}$  to dryness, then proceed as above. To test for  $\text{MeOH}$ , allow 2 cc. of a 2% soln. to stand for 3 min. with 2 cc. 2.5%  $\text{KMnO}_4$  and 0.4 cc. of 50%  $\text{H}_2\text{SO}_4$ , remove excess of  $\text{KMnO}_4$  with 8%  $\text{H}_3\text{C}_2\text{O}_4$  soln., distil, collect the distillate in 20%  $\text{NH}_3$  and treat as before.

S. W.

**Detection and determination of p-saccharin in saccharin and crystalline.** I. M. KOLTHOFF. *Pharm. Weekblad* 62, 548–53 (1925).—For the detection of p-saccharin in saccharin, dissolve 0.25 g. in a soln. of 0.2 g. NaOAc in 3 cc.  $\text{H}_2\text{O}$  by warming. Cool and add 5 drops of AcOH. A sepn. of crystals after 21 hrs. indicates the presence of more than 2% p-saccharin. Crystalline is examd. in the same way except that the addn. of NaOAc is unnecessary. After neutralization of the  $\text{CO}_2\text{H}$  in p-saccharin the  $\text{SO}_2\text{NH}_2$  group still has faintly acid properties. This fact may be taken advantage of for the detection of the p-compd. in crystalline, with nitramine as an indicator. The detn. of p-saccharin may be performed by titration first to methyl red 3 and then to nitramine.

A. W. DOX

**Potentiometric measurement of the reduction of iodate and periodate by iodide ion (MÜLLER, JUNCK) 2. Potentiometric measurement of the reaction between Cl and iodide ion (MÜLLER, JUNCK) 2.**

KNECHT, E. and HIBBERT, EVA: *New Reduction Methods in Volumetric Analysis*. A Monograph. 2nd ed. revised and enlarged. London: Longmans, Green & Co. 134 pp. 8s. 6d. net. Reviewed in *Analyst* 50, 257 (1925).

**Automatic gas analysis by weight.** C. A. HARTUNG. U. S. 1,512,242, June 16. Gas to be analyzed is passed through absorbent material suspended on one arm of a balance. Elec. devices control the balancing of the absorbent material as it increases in wt. and the increase in wt. is automatically recorded.

Apparatus for fume conduction in the Kjeldahl process. W. H. SCOTT. U. S. 1,542,843, June 23.

## 8—MINERALOGICAL AND GEOLOGICAL CHEMISTRY

EDGAR T. WHERRY AND EDW. F. HOLDEN

Origin, occurrence, composition and physical properties of the mineral iddingsite. C. S. ROSS AND E. V. SHANNON. *Proc. U. S. Nat. Museum* 67, No. 7, 19 pp (1925).—Iddingsite is widely distributed in the basaltic rocks throughout the western U. S. It is considered to be a deuteric mineral, that is, it has been produced by processes largely inherent in the magma itself, probably brought about by gases during final cooling. It has hardness 3.5, sp. gr. = 2.8, and 4 cleavages. The *ns.* are variable. An av. of the chem. analyses of 7 samples shows:  $\text{SiO}_2$  39.11,  $\text{TiO}_2$  0.18,  $\text{Al}_2\text{O}_3$  3.29,  $\text{Fe}_2\text{O}_3$  31.49,  $\text{FeO}$  0.96,  $\text{CaO}$  2.28,  $\text{MgO}$  8.05,  $\text{H}_2\text{O}$  8.49,  $\text{H}_2\text{O} - 7.78$ , sum 101.63%. This high summation is due to  $\text{TiO}_2$  being included with  $\text{SiO}_2$ , and  $\text{FeO}$  with  $\text{Fe}_2\text{O}_3$  in certain analyses owing to scarcity of material. The formula calcd. from the analysis is  $\text{MgO} \cdot \text{Fe}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 4\text{H}_2\text{O}$ . L. W. RIGGS

Mineralogy and petrography of Triassic limestone conglomerate metamorphosed by intrusive diabase at Leesburg, Virginia. E. V. SHANNON. *Proc. U. S. Nat. Museum* 66, No. 28, 31 pp (1925).—This study is mainly genetic and petrographic, with optical and crystallographic descriptions of the minerals diopside, datolite, xonotlite, apophyllite, calcite, etc., from low-temp. veins. L. W. RIGGS

Meteorite stone of Colby, Wisconsin. G. P. MERRILL. *Proc. U. S. Nat. Museum* 67, No. 2, 3 pp (1925).—The fall occurred on July 4, 1917. The temp. of the stone was below  $0^\circ$  so that frost immediately formed on its surface on being brought to the air. Microscopic examn. showed the silicate portion of the stone (91.415%) to consist of olivine and enstatite with small quantities of maskelynite and more rarely merrillite. Troilite was rather abundant. Analysis by J. E. Whitfield gave, for the silicate portion:  $\text{SiO}_2$  41.30,  $\text{Al}_2\text{O}_3$  2.83,  $\text{Cr}_2\text{O}_3$  0.50,  $\text{P}_2\text{O}_5$  0.25,  $\text{FeO}$  15.08,  $\text{MnO}$  0.45,  $\text{CaO}$  absent,  $\text{MgO}$  29.40,  $\text{NiO}$  0.21,  $\text{CoO}$  0.02,  $\text{Na}_2\text{O}$  1.11,  $\text{K}_2\text{O}$  0.14; metallic portion: Fe 0.90, Ni 0.07, Co 0.02; troilite: Fe 4.83, S 2.76; sum of the 3 portions, 99.94%. The stone should be classed as an intermediate chondrite. New meteorite stone from Baldwin, Mississippi. *Ibid.* No. 6, 2 pp (1925).—This stone was seen to fall on Feb. 2, 1922. It is chondritic with rather indistinct structure. A thin section shows a fine granular ground with irregularly outlined areas of larger granules, the evident residue of chondrules partially obliterated through metamorphism. The detd. silicate minerals are olivine and an orthorhombic pyroxene with small interstitial areas of plagioclase feldspar. It is classified as a veined white chondrite. L. W. RIGGS

The meteorite of La Colina. E. HERRERO DUCLOUX. *Rev. facultad cienc. quim.* 3, 65-71 (1925).—The meteorite, which fell March 19, 1925, near Buenos Aires, resembles chemically very closely the Heredia meteorite, no. 117 of the series investigated by Farrington. MARY JACOBSEN

Chemical data relative to the aerolite El Toba as a member of the meteoric group of the Campo del Cielo. E. HERRERO DUCLOUX. *Rev. facultad cienc. quim.* 3, 117-24 (1925).—The chem. and microscopical analyses of El Toba, a uraninite of 4210 kg. and a no. of other siliceous and metallic meteorite fragments found in various points of the Campo del Cielo establish their common origin from a single gigantic meteorite. MARY JACOBSEN

Limestone resources of Illinois. FRANK KREY AND J. E. LAMAR. Ill. State Geol. Survey, *Bull.* 46, 17-371 (1925).—This detailed report discusses the methods of sampling and testing limestone road materials, quarry practice, quarries and quarry sites in Illinois, the limestone resources of Ill. by counties, and the uses of limestone. The phys. properties and chem. compn. of all Ill. limestones that have been tested are given in tabular form. E. F. H.

The results of tectonic pressures as shown at the boundary zones between rock salt and carnallite. A. KIESEL. *Kolloid* 18, 73-7; *Chem. Zentr.* 1924, I, 2237.—Examn. of a no. of potash deposits has shown that the strata are most distorted, usually by folding rather than slippage, at places where a rock-salt layer adjoins one of carnallite, the  $\text{K}_2\text{O}$  being also high in these locations. The surface zone of the carnallite near the rock salt has in general a conglomerate type of structure. WM. B. PLUMMER

The geological function of thermal springs. PIERRE URBAIN. *Rev. sci.* 63, 71-5 (1925).—A brief discussion of the problems of hydrothermal metamorphism.

A. PAPINEAU-COUTURE

Contents of oxygen in the ocean on both sides of Panama. J. SCHMIDT. *Science* 61, 592-3(1925).—O was detd. at a station in the Atlantic and at a station in the Pacific. At the surface, the water at both stations is nearly satd. with O. At a depth of 50 m. the Atlantic water is still satd. with O while the Pacific water has only 0.25 as much O as at the surface, and at a depth of 150 m. only 0.1 as much. The min. was found at a depth of 400 to 500 m., where the Atlantic still contains 40 to 50% of the O at the surface, but the Pacific contains "practically no O at all." L. W. RIGGS

Absolute determination of the age of radioactive minerals. W. EIREL. *Naturwissenschaften* 13, 362-4(1925); cf. Ellsworth, C. A. 19, 1241. B. J. C. v. d. H.

Various types of pyrites in coal (LOMAX) 21. Occurrence of methane in brown-coal mines (FLEISSNER) 21.

## 9—METALLURGY AND METALLOGRAPHY

D. J. DEMOREST, R. S. WILLIAMS

The availability of the Gröndal-Franz flotation process for natural occurring tetra-hedrite. GLATZEL. *Metall u. Erz* 22, 1-11(1925).—By special adaptation, the Gröndal-Franz flotation process can be used for recovery of very finely pulverized tetrahedrite. C. G. KING

Development and operation of a fifty-gram flotation machine. J. F. GATES AND L. K. JACOBSEN. *Eng. Mining J.-Press* 119, 771-2(1925).—A description of a machine designed at the Bureau of Mines Intermountain Expt. Station, Utah, for rapid work where only small quantities of pulp are available. A complete test can be run in 15 min., with results which compare well with those of large machines. A. BUTTS

Metallurgy of magnesium. M. MIRVAK AND ALLISON BUTTS. *Eng. Mining J.-Press* 119, 843-6(1925).—A summary of published information. A. B.

The treatment of platinum ores. B. W. HOLMAN. *Mining Mag.* 32, 283-5 (1925).—Pt cannot be caught by amalgamating plates nor dissolved in any suitable solvent. Fineness of the Pt particles and leanness of the ores (0.0057 and 0.00034% Pt given in 2 analyses) preclude ordinary concn. methods. In South Africa it is hoped to catch the Pt on blankets, but a recovery of 40% in this way can hardly be exceeded. Certain devices could be made to reject considerable gang without much loss of Pt, thus giving an enriched slime. A new method of treatment is needed for good recovery. Smelting with Ph appears economically feasible. A. BUTTS

Experiences in the removal of antimony from raw lead by dry processes. B. GEORGE. *Metall u. Erz* 22, 27-34(1925).—Sb is removed from raw Pb by the use of PbO as an oxidizing agent. The results of 13 exptl. batches are discussed in relation to com. practice. Too great an excess (50%) of PbO above the theoretical lengthens the time and is inadvisable. Use of a slight excess gives economical results. C. G. KING

Bwana M'Kubwa—a potential copper producer. G. L. WALKER. *Eng. Mining J.-Press* 119, 837-42(1925).—A large plant is being built in Northern Rhodesia to treat the ore of the Bwana M'Kubwa and N'Kana mines, using a new process developed by Minerals Separation, Ltd., after several years of lab. work and operation of a 10-ton pilot mill, and called by them the "Metals Production Process." The vital feature of the process is the conversion of all forms of Cu in mixed Cu ores to oxides readily sol. in a soln. of  $(\text{NH}_4)_2\text{CO}_3$  in the presence of O. The ore is crushed to  $\frac{1}{2}$ -1 in. and passed through a rotary kiln, which heats it to 400-450° in about  $\frac{1}{2}$  hr. After preheating the ore goes to a cylindrical reducing furnace fitted with an internal spiral for control of the time of contact, where it meets a counter-current stream of producer gas. In 20 min. the reducing action is complete. The ore is then crushed further to  $\frac{1}{8}$  in. and leached in tanks with a soln. that contains primarily 5%  $\text{NH}_3$  and 4%  $\text{CO}_2$ . A leaching and washing cycle yields an extn. of 90% of the Cu in 3 to 7 days. CuO is pptd. from the soln. with steam as usual in ammonia leaching. The oxide is then reduced to metal by smelting with tar, followed by the usual poling. The product is 99.85% Cu. Sulphates and all other types of Cu minerals are easily dealt with. The producer-gas atm., together with control of temp. and time, are vital factors. The plant will have ten 1000-ton leaching tanks and produce 10,000 tons of Cu annually. A. BUTTS

The deoxidation of steel. C. H. DESCH. *J. West of Scotland Iron & Steel Inst.* 32, 40-4; discussion, 44-9.—The chemistry of deoxidation of steel is not fully understood. Blowholes in mild steel weld together on rolling or forging, but not so in high-C or

special steels. It is difficult to deoxidize steel when much O has been present; even in an elec furnace it is hard to get sound castings when much rusty scrap has been charged. The Swedish Bessemer process blows pig iron low in Si and high in Mn; some Mn is always present throughout the blow, and much of this steel is made without using a deoxidizer. Pure Fe contg up to 0.8% O can be readily forged or rolled, the bad effects of O appear only in the presence of a third constituent. Mn is usually necessary for proper deoxidation even when other agents are used. Steel can be successfully deoxidized by Mn alone, but not by Al alone. Mn not only removes O, but probably also causes particles of slag to coagulate to larger globules. JOSEPH JEFFERSON: Elec steel cannot be "killed" with Mn alone, Si is required, even though Mn has been continually present in the bath. The bad effect of using excess scrap in charges does not seem to be due to the oxide of Fe. S. L. ROBERTSON: The same results as obtained in the Swedish Bessemer process would be obtained by adding ferro-Mn during the blow.

A. BUTTS

Calcium carbide as a deoxidizing agent. ANON. *Chem.-Zig* 49, 456-7(1925).—The oxidizing and reducing agents for cast iron and steel are briefly reviewed. The analysis of 2 castings is given and it is shown that  $\text{CaC}_2$  took no part in the reduction of FeO. This is explained by its high m p.

J. T. STERN

Steel castings. E. WAACK. *Teknisk Ukeblad* 72, 98-100, 111-2(1925).—An illustrated review of the modern methods and app.

C. H. A. ROBAK

Influence of nickel and chromium upon gray and malleable cast iron. L. NORTH-COTT. *Bull Brit Cast Iron Res Assoc* 1925, No 8, 5-8.—Conclusion of a brief complete summary, with bibliography. Cf. C. A. 19, 1242.

A. BUTTS

The growth of modern theories of fatigue failure. H. C. DEWS. *Metal Ind* (London) 26, 551-3(1925).

E. H.

Recent developments in tensile testing. J. V. HOWARD AND S. L. SMITH. *Proc. Roy Soc* (London) 107A, 113-25(1925).—Up to certain limiting stress extension is proportional to the applied load. When this stress is exceeded this proportional elasticity is lost but non-proportional elasticity is retained; then the removal and re application of the load causes a loop to be traced in the recorded load extension diagram. Loop area increases with permanent set and when the 2 factors are plotted against each other a smooth or "normal" curve results. Factors influencing formation of loops have been studied with especial reference to variation in compn of steel. The total stretch of the test-piece is made up of a proportionally elastic portion and a non proportionally elastic portion, called the "recoverable slip." Recoverable slip is proportional to loop area. It depends only on the stress and is independent of the cross-section of the specimen. Mean loop width is a measure of recoverable slip. The ultimate cause of rupture is permanent set or plastic deformation and not the total amt. of work expended in producing this deformation. When a loop is traced an internal disturbance is set up in the metal which produces permanent set and therefore final rupture. A "quality factor" for steels is proposed, which is defined as the stress in tons per sq in necessary to produce a standard loop width of 0.0015 in., using test-pieces of 5 in. gage length. A steel having a low quality factor will give large loops and conversely. The influence of C content and heat treatment on the quality factor was studied for various C steels and for certain alloy steels. The quality factor varies with C content of steels, reaching a max. at 0.6% C in heat-treated steels and approaching a min. at the same compn. in annealed steels. Ni up to 3% shows no effect on the quality factor, while correctly heat-treated Ni-Cr steels contg 0.8 to 1.2% Cr had a factor 1.6 times that of plain C steel of the same C content. Variations in elastic limit were studied with varying P and C contents as well as with varying Ni and Ni-Cr content in annealed and heat-treated steels. The effect of resting for periods of 15 to 90 days on overstrained steels is summarized as follows: (i) Annealed (pearlitic) hypoeutectoid steels, including pearlitic Ni steels, completely recover their property of proportional elasticity with rest. The limit of proportional elasticity after rest is the max. load previously applied. (ii) Sorbitic (heat-treated) C steels of all compns. have no such power of recovery. On re loading after rest, the load extension line was curved and a loop was traced on the removal of the load. (iii) C steel of eutectoid compn. does not recover, whatever its previous heat treatment. No recovery of proportional elasticity takes place while the metal remains under load for 18 days. The normal curve of loop area against permanent set indicates the heat treatment which the steel has undergone. D. P. McF.

The thermal and electric conductivities of some aluminum alloys. HAKAR MASUMOTO. *Sci Repts Tohoku Imp. Univ* 13, 229-42(1925).—Simidu's method (C. A. 12, 467) consisting of passing an elec current through a rod of uniform section while keeping both ends at a const temp., is used. The axial distribution of temp. in the rod

becomes parabolic in the stationary state, providing no lateral loss of heat takes place. This loss is reduced to zero by the use of a guard tube around the rod, the axial distribution of temp in which is parabolic and the same as that in the test specimen. The thermal and elec. conductivities of Al alloys are much lower than those of pure Al, and the greater the quantity of the other constituents, the greater is the decrease of the two conductivities. Mn and Cr have a great influence on these properties. Annealing generally increases both conductivities. The Al alloys contg a large amt of Si (12%) are greatly affected by annealing, whereas in alloys contg Zn (up to 20%) annealing has but slight effect. Quenching usually diminished the two conductivities of Al, which indicates solution of the other constituents in Al. Aging the specimens usually decreases both conductivities. Both pure Al and its alloys in the cold-drawn and annealed condition have much greater values for the cond than those in the chill cast and annealed states, resp. Although there was a large variation in the values of the thermal and elec. conductivities in the Al alloys studied, their product is nearly const. The mean of the product for Al alloys is  $0.165$  or  $6.91 \times 10^{10}$  C G S E M U while the mean for the product for Al and Mg is  $0.158$  or  $6.62 \times 10^{10}$  C G S E M U. The theoretical value at  $30^\circ$  being  $6.99 \times 10^{10}$  C G S E M U. In general the smaller the values of the two conductivities the greater will their product be. M concludes that in a good conductor, heat is mainly conducted through free electrons, that due to atoms being negligibly small. As the cond decreases, the conduction due to the atoms becomes sensible while the electricity is always conducted by free electrons, which results in a small increase of the product of the two conductivities. J. H. P.

The equilibrium diagram of the binary alloys of antimony and bismuth. BUNYARO OTANI. *Sci. Repts. Tohoku Imp. Univ.* 13, 293-7 (1925).—The elec resistance method was used for the study of the solidus, while the method of Konno (*C. A.* 15, 2611) and Ishihara (*C. A.* 19, 926) was used in studying the liquidus. The exptl results show that this system belongs to the ordinary type of solid solution. The following figures give % Bi in the alloy and liquidus and solidus temps in degrees C. 100, 270.—; 80, 400, 288; 60, 482, 311; 40, 514, 362; 20, 593, 447, 10, 610, 522, 0, 629.—. J. H. PERKY.

The effect of acidity and oxidation capacity on corrosion of metals and alloys in acid mine water. R. E. HALL AND WM H. TRAUER. Carnegie Inst., *Tech. Bull.* 15, 62 pp (1924).—Electrolytic corrosion tests of Cu, Zn and Sn in acids and soln. of ferrous and ferric salts and comparison with simple immersion tests showed that the use of a current was inadvisable except where passivity or pitting was to be studied. Corrosion rates are given for 23 metals and alloys in solns. of various H-ion concn. and oxidation capacities. Corrosion of Zn, Sn and especially Cu in mine waters is proportional to the concn. of ferric ion. A simple electrometric titration method for detg. ferrous and ferric ion concns is described. The electrode potentials of alloys were observed and found to change but little in 25 hrs. except in the cases of Ni, rustless steel, nichrome, Al-Mn and Al-Si alloys. Corrosion in bicarbonate waters depends upon dissolved O.

E. L. CHAPPELL

Furnace heating (SARJANT) 21. The heterogeneous  $H_2O$  and  $CO_2$  dissociation equilibria over Fe and its oxides (HOFMANN) 2.

Treating copper ores. W. E. GREENAWALT. U. S. 1,542,934, June 23. A Cu sulfide concentrate is roasted, leached to ext. a portion of the Cu and the leached residue is smelted to form a mat contg the residual Cu. The mat is crushed and added to a new sulfide concentrate for continuing the process. Cf *C. A.* 19, 1399, 1400.

Treating copper and lead ores. W. E. GREENAWALT. U. S. 1,542,935, June 23. Cu and Pb ore contg. precious metals is smelted to a mat, the mat is crushed and roasted and leached with dil. acid to ext. a portion of the Cu, the Cu soln. is electrolyzed to deposit Cu and regenerate the acid soln. and the regenerated acid soln. is returned to the mat and these operations are continued until the Cu is sufficiently extd. from the roasted mat. Then the residue contg. precious metals, a small quantity of residual Cu and the Pb ore is smelted to obtain a Pb bullion contg. most of the precious metals and a Pb-Cu mat contg. a minor portion of the precious metals. The Pb-Cu mat thus obtained is added to a new Cu ore charge and the cycle is repeated.

Treatment of sulfide ores. E. A. ASHCROFT. Can 247,211, Mar. 3, 1925. Sulfide ores are subjected to the action of  $SCl_2$  to form metallic chlorides, which are then sepd. from the unconverted constituents.

Reduction of iron ore. RAGNVALD STØEREN and REIERT JOHANSON. Norw. 41,029, March 9, 1925. The ore is reduced by  $H_2$  passing in counter-current through the preheated charge. Mech. and elec. features are specified.

Treating titaniferous iron ores. C. R. WHITTEMORE. U. S. 1,542,350, June 16. The Fe in the comminuted ore is converted into sponge Fe, *e. g.*, by heating with charcoal at 900–1050°, and the reduced ore, without having been subjected to fusion or sintering, is leached with sufficient solvent, *e. g.*, a  $\text{FeCl}_3$  soln. at 80°, to dissolve the Fe.

Charging ore, fuel and flux into smelting furnaces through the air blast tuyères. H. HENRICH. U. S. 1,542,245, June 16. Mech. features.

Apparatus for roasting and smelting ores. J. M. SAMUEL. U. S. 1,542,966, June 23.

Rabble furnace for roasting ores. A. V. LEGGO. U. S. 1,542,150, June 16.

Siemens-Martin furnace. P. OSTENDORF. U. S. 1,541,843, June 16.

Crucible. J. H. DEPPER. U. S. 1,542,784, June 16. A deoxidizing or purifying material in the form of a ferro alloy forms a coating or plug at the bottom of a crucible for melting steel or other metals so that it melts and associates with the metal in the crucible.

Plugging crucibles. E. F. BEGYRUP. U. S. 1,542,598, June 16. The bottom of a crucible which may be used for holding molten steel is closed by a plug of steel or other metal of a size which will melt out in the desired time.

Apparatus for purifying molten metals. R. F. AGRICOLA. U. S. 1,541,778, June 16. The app. is adapted for treating molten Al or other metals with gases, vapors and fluxes, etc.

Treating titanium-nitrogen compounds. TITAN CO. A.-S. Norw. 40,986, March 2, 1925. The Ti-N compds are treated with  $\text{H}_2\text{SO}_4$  under increased pressure. The quantity of  $\text{H}_2\text{SO}_4$  should not exceed considerably that necessary for combining with the constituents of the raw material excluding the Ti. This element is then obtained as an insol. ppt. while the impurities as well as the Fe and N are obtained mainly in the form of sol. sulfates, which can be removed by washing.

Pickling steel sheets. J. T. HAY. U. S. 1,542,451, June 16. Chrome steel sheets are pickled in a soln. contg.  $\text{H}_2\text{SO}_4$  5% and  $\text{HCl}$  2% and are then subjected to the action of 10%  $\text{HCl}$ , washed and treated with  $\text{HNO}_3$ .

Recording apparatus for thermometric tests of steels, etc. P. CHEVENARD. U. S. 1,542,216, June 16.

Alloy. N. L. OLSON. Can. 247,488, Mar. 10, 1925. A heat-resistant alloy contains Ni, Cr, Fe, C in excess of 2% and a small quantity of Si, Al and Mn.

Metals or alloys by silico-thermic reduction. S. D. DANIELT and B. M. S. KALLING. U. S. 1,543,321, June 23. In producing metals or alloys of low C and Si content, an alloy of relatively high Si content is oxidized with a metal oxide, *e. g.*, Cr oxide in a silicate slag, to produce a silicate slag relatively low in metallic oxides and a metallic silicide low in C and relatively high in Si. The silicide is then treated with a metallic oxide such as Cr oxide to produce a metal relatively low in C and Si and a silicate slag relatively high in metallic oxide and the metal is sepd.

Iron alloy. G. A. DRYSDALE. U. S. 1,542,440, June 16. Homogeneous, dense, tough, malleable castings are formed of Fe contg. about 0.5% S and less Mn than S, over 1.5% C and total metalloids sufficiently low to produce a white casting which has a tensile strength of over 50,000 lbs. per sq. in.

Nickel-iron alloys. P. GORDON. U. S. 1,542,232, June 16. Alloys which may be used for turbine blades, valves, etc., are formed of Ni 25–40, Cr or other metal of the Cr group 8–15, Mn 0.5–5, C 0.3–1% and the remainder Fe. U. S. 1,542,233 specifies Ni 20–40, Cr 10–15, Mn 1–5, C 0.2–1 and the remainder Fe, to produce heat-resistant, non-corrodible, ductile, malleable alloys adapted for wire-drawing and forging. Cf. C. A. 18, 1811.

Apparatus for separating magnetic from non-magnetic materials. L. J. INGOLFSRUD and WM. H. SOULE. Can. 247,409, Mar. 10, 1925.

Welding aluminium. S. A. WILTSIE. U. S. 1,542,753, June 16. Special features of localized heating.

## 10—ORGANIC CHEMISTRY

CHAS. A. FOUILLER AND CLARENCE J. WEST

Symbolism in organic chemistry. P. BRUYLANTS. *Bull. sci. acad. roy. Belg.* 10, 680–97(1924).—A discussion of the influence of present and past systems of nomenclature and classification upon the development of the science. WM. B. PLUMMER.

Isomerization phenomena among olefinic substances. P. BRUYLANTS. *Bull. sci. acad. roy. Belg.* 10, 492–503(1924).—A general discussion, in which it is pointed

out that migration of the double bond will usually occur if the groups on each side of it possess markedly different residual affinities. Thus in the synthesis of  $C_6H_5$ , the isomer  $MeCH:CHMe$  is formed almost exclusively. The strength of the residual affinities of homologous groups is in some cases a periodic function of the no. of atoms in the chain; this is shown by the fact that  $PhCH:CHCH_2CO_2H$  and  $PhCH_2CH:CHCO_2H$  are, resp., the stable and unstable isomers, while by adding a  $CH_2$  the relation is reversed,  $PhCH_2CH:CHCH_2CO_2H$  and  $PhCH_2CH_2CH:CHCO_2H$  being, resp., unstable and stable.

WM. B. PLUMMER

The action of sulfuric acid and sulfuric anhydride on acetylene dichloride. HECYOR LEPOUSE. *Bull. soc. chim. Belg.* 34, 133-42(1925).—Ether isomeric  $CHCl:CHCl$  reacts with 50% oleum (200 g/mol) or with  $SO_3$  to give approx. 80% of  $HO_2SCHClCHO$  (I), obtained as the Ba salt after diln. of the reaction mixt. with  $H_2O$  and addn. of  $BaCO_3$ . The K salt, prepd. by double decompn. with the Ba salt, m. 123-4°, its aldolxime decomp. at 200°. I is oxidized by  $H_2O_2$  to  $HO_2SCHClCO_2H$ , while steam distn. of I in the presence of 60%  $H_2SO_4$  gives  $CH_2ClCHO$ .

WM. B. PLUMMER

Preparation of alcohol by catalytic reduction of aldehyde. K. NEGOSHI. *Report Osaka Ind. Research Lab. (Japan)* 5, No. 6, 1-361(1924).—Optimum conditions for the manuf. of alc. by catalytic reduction of  $AcH$  by Ni are reported.  $AcH$  was prepd. by oxidation of alc. by  $CrO_3$  and purified by converting it to  $MeCH(OH)NH_2$  which is decompd. and distd. Its purity was 99.3% according to Bourcart's method, and 97.25% according to Seyewetz and Bardin's method. The most efficient Ni catalyst is obtained when pumice is soaked with  $Ni(NO_3)_2$  to make it 30% with respect to Ni and heated at 500° in H at a rate of 100 cc. per min. for 6 hrs. The best reduction temp. for aldehyde by Ni prepd. from  $Ni(NO_3)_2$  is 140°, while that by Ni prepd. from  $NiO$  is 100°. The best rate for passing the  $AcOH$  is 60-70 cc. per min. for Ni prepd. from  $Ni(NO_3)_2$  and 150-70 cc. for Ni prepd. from  $NiO$ . The greater the excess of H used during the reduction, the more alc. will be formed. With a 7-fold excess of H, 90% alc. was obtained.

S. T.

Action of phosphorus pentachloride on certain aldehydes and ketones. BOURQUEL. *Bull. soc. chim.* 35, 1629-33(1924).

E. J. C.

Laboratory experiments. TOMAS DE PALACIO. *Afinidad* 5, 31-5(1925).—Boiling  $PROH$  reacted with gaseous  $HCl$  in presence of 50%  $CaCl_2$  to form a water-insol. oil, b. 86-8°,  $d_{44}^{20}$  0.8723,  $d_{44}^{25}$  0.8668,  $n_D^{20}$  1.3773.  $Cl$  was not detd.

M. J.

Reactions of triethylphosphine. J. N. COLLIER. *J. Chem. Soc.* 127, 964-5(1925).—In the prepn. of  $PEt_3$  from  $PCl_3$  and  $Et_2Zn$ , diethylphosphinic acid,  $Et_2PO_2H$ , b. about 320°, solidifies in a freezing mixt., results as a by-product; its *Ag* salt,  $C_4H_{10}O_2P_2Ag$ , long, silky needles, is stable in boiling  $H_2O$ .  $PEt_3$  and  $PCl_3$  or  $POCl_3$  react with great violence, free P resulting;  $SiCl_4$  and  $S_2Cl_2$  react similarly, yielding free Si and S.  $SnCl_4$  or  $ZnCl_2$  does not react violently and gives a double salt.  $PEt_3$  may be boiled with  $PhCl$  or  $PhBr$  without reaction;  $PbI_2$  reacts very slowly, giving the complex,  $PEt_3 \cdot PbI_2$ , 4-sided plates.  $(CH_3)_3Br$  gives a similar complex. Chloral gives metachloral; chloral hydrate in dry  $Et_2O$  gives an oil, whose chloroplatinate analyzes for  $2(PEt_3 \cdot C_2H_5Cl_2O_2) \cdot PtCl_4$ . A soln. of  $HCHO$  dissolves  $PEt_3$ ; addn. of  $HCl$  and  $PtCl_4$  gives the compd.  $2(PEt_3 \cdot CH_2OCl) \cdot PtCl_4$ .  $AcH$  gives a similar compd.

C. J. WEST

Some aromatic chlorovinylarsines. A. F. HUNT AND E. R. TURNER. *J. Chem. Soc.* 127, 996-9(1925).— $C_6H_5$  is slowly absorbed by a soln. of  $AlCl_3$  in  $PhAsCl_2$  to give, after treatment with ice and  $HCl$ , phenyl- $\beta$ -chlorovinylchloroarsine,  $b_D$  140-5°, which slowly acquires a violet color if not completely purified, and phenyl- $\beta, \beta'$ -dichlorodivinylarsine (I),  $b_D$  155-60°, with a nauseating fishy odor; this yields with  $AgNO_3$  an addn. product  $2I \cdot AgNO_3$ , m. 142° (decompn.). I also results from  $PhMgBr$  and  $(ClCH_2)_2AsCl$ . I forms cryst. add. products with  $HgPtCl_4$  and  $HgCl_2$  and slowly combines with  $MeI$  under pressure at 100° to give a gummy methiodide. If, during the absorption, the soln. is not cooled, there results  $C_6H_5$  and  $ClCH:CHAsCl_2$ .  $AlCl_3$  in cold  $PhAsCl_2$  deposits the compd.  $PhAsCl_2 \cdot AlCl_3$ , pale yellow, from which  $HCl$  regenerates  $PhAsCl_2$ ; if the soln. is allowed to stand more than a few hrs., a mixt. of products,  $b_D$  130-270°, results.  $PhC:CH$ ,  $AsCl_3$  and  $AlCl_3$  gave a yellow amorphous solid of indefinite m. p.  $PhC:CH$  and  $AsCl_3$ , heated 4 hrs. at 110°, gave a mixt. of  $\alpha$ -chlorostyryldichloroarsine, yellowish green oil,  $b_D$  103-10°, and  $\alpha, \alpha'$ -dichlorodistyryldichloroarsine, olive-green, viscous liquid,  $b_D$  170-5°. Neither possessed an unpleasant odor or vesicant properties.

C. J. WEST

Constitution of the Grignard magnesium compounds. II. JAKOB MEISENHEDIER, JOH. CASPER, E. PIPER AND U. SCHOLTZ. *Ann.* 442, 180-210(1925); cf. C. A. 15, 3978—Hess and Reinboldt (C. A. 16, 409) have reported that  $BzH$  (I) and alkyl

Mg halides give the normal reaction product (phenylalkylcarbinols) only when the reaction mixt. is not heated before decompn. with  $H_2O$ ; if the mixt. is heated in  $Et_2O$  or better in  $C_6H_6$  for a short time, up to 75% of the I is reduced to  $PhCH_2OH$  (II). Since these results were directly opposed to those reported by M., the work has been repeated and extended. First the reaction of  $(CH_3)_2O$  was studied (cf. Grignard, *Bull. soc. chim.* 29, 944(1903)) ( $CH_3)_2O$  and  $EtMgBr$  in  $Et_2O$  at  $-20^\circ$  give the compd.  $EtMgBr \cdot C_2H_5O$  0.25  $Et_2O$ ; on treatment with acid this liberates the  $C_2H_5O$ , which then reacts with the  $MgBrOH$  to give  $HOCH_2CH_2Br$ . In a high vacuum the  $Et_2O$  is removed in a few hrs., giving the compd.  $EtMgBr \cdot C_6H_5O$ , but in an ordinary vacuum there finally results the compd.  $C_6H_5O \cdot MgBrOH$ . If the reaction mixt. is heated on the  $H_2O$  bath there results the compd.  $EtCH_2CH_2OMgBr$ , which is stable in vacuum. In a study of the dectn. of II as the *p*-nitrobenzoate, it was found that  $PhEtCHOH$  (III), heated with  $O_2NC_6H_4COCl$  in abs.  $Et_2O$  for 15 hrs., gives 1-phenyl-1-chloropropane, *b*<sub>p</sub> 50-52°; if the 2 components are heated alone, there is also formed 20% of the carbonyl *p*-nitrobenzoate, *m* 59-60°. 1-Phenyl-1-chloro-3-methylbutane was similarly prepd. II is quant. esterified by heating with *p*- $O_2NC_6H_4COCl$  for 1-2 hrs. or by boiling the concd.  $Et_2O$  soln 16 hrs. A method for the dectn. of II is given based on this.  $EtMgX$  and I in mol. amts. in  $Et_2O$  at  $0^\circ$ , immediately decompd. with 10% HCl after mixing, give 20-40% unchanged I, some III, but no II. After standing 3 hrs. at room temp., there is formed 0-3% II, the amt. of I recovered is decreased to 10-20% and the amt. of III formed is correspondingly increased. After 24 hrs. standing, only 4-6% I is recovered and 0-9% II is formed. If the  $Et_2O$  is removed and the product heated with  $C_6H_6$ , there results 10-20% II and 10-25% high boiling residue. The use of  $EtMgI$  appears to favor the formation of II. If an excess of  $EtMgX$  is used, no II results after 24 hrs. but with an excess of I, there results 30-40% of II, no I is recovered and the high-boiling residue is considerably increased. The use of  $Et_2O$ -free  $EtMgX$  ( $C_6H_6$  as solvent), if the product is immediately decompd., gives no II and a recovery of 30-35% I; after 23 hrs. standing, the yield of II is 10-15%, after 24 hrs. 15-22%, while after heating, the yield of II is about the same but the high boiling products are increased. III and  $EtMgBr$  in  $Et_2O$  give some unsatd. hydrocarbon, while in  $C_6H_6$  the main product is unsatd. III and  $EtMgI$  in  $Et_2O$  give the cryst. compd.  $C_6H_5OMgI \cdot Et_2O$ ; the  $Et_2O$  is only slowly lost in vacuum; it is not changed by heating with  $C_6H_6$ .  $BzH$  and  $EtMgI$  give a compd. of similar compn. By the use of iso-BuMgBr the yield of II is higher than with  $EtMgBr$ .  $MgBr_2$  and I in  $Et_2O$  give the compd.  $MgBr_2 \cdot 2I$ , *m*. 153-5°.  $PhCH:CHCHO$  and  $EtMgBr$  give the compd.  $PhCH \cdot CHCH(OMgBr)Et$ , which loses  $Et_2O$  in vacuum at  $60^\circ$ . This product, decompd. with  $NH_4Cl$  soln., gives 1-phenyl-1,3-pentadiene. Isobutylstyrylcarbinyl *p*-nitrobenzoate, pale yellow, *m* 103-4°. Unlike I,  $PhCH \cdot CHCHO$  does not appear to be reduced to the corresponding alc. by the Grignard reagent.

C. J. WEST

Organic compounds of lead. GEORGE CALINGAERT. *Chem. Reviews* 2, 43-83 (1925)—A review with 36 references. All the known Pb org. compds. are listed with their phys. properties.

C. J. WEST

Mechanism of the reaction in the catalytic reduction of oximes. V. GULEVICH. *Ber.* 58B, 798(1925)—Reply to Rosenmund and Jordan, *C. A.* 19, 1412.

C. A. R.

The thermochemistry of the butenonitriles. P. BRUYLANTS AND A. CHRISTIAEN. *Bull. soc. chim. Belg.* 34, 144-50(1925); cf. *C. A.* 19, 37.—The heats of combustion have been detd. for the stereoisomeric crotononitriles  $MeCH:CHCN$ , *b*<sub>m</sub> 107.9-8.0° (I) and *b*<sub>m</sub> 120.8-9° (II), and for  $CH_3 \cdot CHCH_2CN$  (III) and  $CH_3CH_2CHCN$  (IV) as,

resp., 571.0, 572.9, 574.0, and 580.6 kg. cal./mol. Comparing I and II on this basis, II should be the unstable isomer and hence the nitrile of isocrotonic acid. However, the facts that *n* of II is higher than *n* of I and that II is the higher boiling isomer (crotonic acid boils 5° higher than the *iso*-form) lead to the opposite conclusion, so that the question cannot be considered closed.

WM. B. PLUMMER

Tautomerism of dyads. III. The effect of the triple linking on the reactivity of neighboring atoms. EDITH H. INGOLD. *J. Chem. Soc.* 127, 1199-1206(1925); cf. *C. A.* 18, 4165.—The  $\beta$  H atom in  $CH \cdot CCO_2R$  is so reactive that it not only undergoes Claisen condensations, with loss of  $H_2O$ , with compds. such as  $(CO_2Et)_2$ , but also undergoes the Michael addn. reaction with, e. g., *Et* fumarate. The  $-CO_2Et$  group in these esters definitely enhances the reactivity of the acetylenic H atoms. *Me propiolate* (I), *b*<sub>m</sub> 102°. Alc.  $EtONa$  and  $CH \cdot CCO_2Et$  give *Et*  $\beta, \beta$ -diethoxypropionate, *b*<sub>m</sub> 206°. The Claisen reaction between I and  $(CO_2Me)_2$  gave, after reduction of the products,  $(CH_3CO_2H)_2$ , glutaric acid,  $(CO_2H)_2$ , and catechol. The *Et* ester and  $BzOEt$  gave  $PhC \cdot CCO_2Et$  and  $PhCH_2CH_2CH_2CO_2H$ . The Michael reaction with  $CH \cdot CCO_2Et$

and Et fumarate gave butane- $\alpha,\beta,\delta$ -tricarboxylic acid and muconic acid. AmC CH does not condense with  $(\text{CO}_2\text{Et})_2$ . Et tetrolate and  $(\text{CO}_2\text{Et})_2$  gave only resinous products and  $(\text{CO}_2\text{H})_2$ . These and earlier results indicate that the acetylenic linkings are governed by special principles distinct from (and, in some respects, opposite to), those which control the corresponding phenomena in which ethylenic linkings are concerned.

C. J. WEST

Chromic acid oxidation in relation to the molecular structure of stearolic and tariric acid derivatives. LOUIS-JACQUES SIMON *Compt. rend.* 180, 1405-7 (1925).—Detn. of C by oxidation with  $\text{AgCrO}_4$  at  $100^\circ$  gave results agreeing closely with the theoretical, but with  $\text{CrO}_3$  at  $100^\circ$  the results were always low. Let  $\Delta$  be the no. of C atoms not attacked by  $\text{CrO}_3$ , i. e. =  $[(\% \text{ C theoretical} - \% \text{ C by } \text{CrO}_3) / \% \text{ C theoretical}] \times (\text{no. C atoms present})$ . Among most of the compds. studied  $\Delta$  varies between 0.9 and 1.5, certain regularities being observable, e. g., the isomers oleic and elaidic acids gave for  $\Delta$  1.32 and 1.19, resp., while the isomers stearolic and tariric acids gave 1.30 and 1.19, showing the same relation to exist between each pair of isomers. Data are given for a no. of similar cases. In general  $\Delta$  as detd. above gives some insight into the relative structures of 2 isomers if comparative data are available. Cf C. A. 19, 1851.

WM. B. PLUMMER

Thiophosphoryl chlorides of the general formulas  $\text{SP}(\text{OR})_2\text{Cl}_2$  and  $\text{SP}(\text{OR})_2\text{Cl}$  and derivatives of the pentabasic thiophosphoric acid  $(\text{HO})_5\text{PSH}$ . W. AUTENRIETH AND WILHELM MEYER. *Ber.* 58B, 840-7 (1925).—It has been shown (*Ber.* 31, 1094 (1898)) that  $\text{PSCl}_2$  in aq. NaOH reacts readily with phenols, thiophenols and primary aromatic amines. With phenols, 1, 2 or 3 of the Cl atoms are replaced, depending on the conditions, by the phenol residue. With dil. NaOH (10%) and in the cold are formed  $\text{SP}(\text{OPh})_2\text{Cl}_2$  and  $\text{SP}(\text{OPh})_2\text{Cl}$  and with more concd. alkali at the boiling temp. is obtained  $\text{SP}(\text{OPh})_3$ , but the latter is not formed under the same conditions from the 1st two; even with much PhOH in boiling 25-30% NaOH  $\text{SP}(\text{OPh})_2\text{Cl}_2$  does not go beyond the stage of  $\text{SP}(\text{OPh})_2\text{Cl}$ , and the same is true on heating with PhOH without NaOH in a sealed tube; only by fusion of the di- or monochloride with  $\text{PhONa}$  at  $180$ - $200^\circ$  is the neutral ester obtained. These chlorides are remarkably stable towards  $\text{H}_2\text{O}$ ,  $\text{Na}_2\text{CO}_3$  and aq. alkalis but they react easily with  $\text{NH}_3$ ,  $\text{PhNH}_2$  and  $\text{PhNHNH}_2$ .  $\text{SP}(\text{OPh})_2\text{Cl}_2$  heated with  $\text{PhNH}_2$  and aq. NaOH gives  $\text{SP}(\text{OPh})(\text{NHPh})_2$  but if 1 mol.  $\text{PhNH}_2$  is added dropwise, without heating, to a fine suspension of the dichloride in much dil. NaOH, there seps. a small amt. of a mixt. of the dianilide and  $\text{SP}(\text{OPh})(\text{NHPh})_2\text{Cl}$ , while from the alk. soln. acids ppt. *Ph. thiophosphate dianilide*,  $(\text{PhNH})_2(\text{PhO})(\text{HO})\text{PSH}$  (I), which titrates with 0.1 N alkali as a monobasic acid and with I gives 2 mols.  $\text{PhNH}_2$  and di-*Ph. disulfidodiphosphate dianilide*,  $[\text{PhO}(\text{PhNH})\text{P}(\text{O})\text{S}]_2$  (II); all attempts to disrupt the S-S union with nascent H have failed. Heated alone, I slowly gives off  $\text{H}_2\text{S}$  from  $180^\circ$  up, with formation of  $\text{OP}(\text{OPh})(\text{NHPh})_2$ , also obtained quant. from  $\text{OP}(\text{OPh})_2\text{Cl}_2$  shaken with 5 mols. of satd. aq.  $\text{PhNH}_2$ . I also slowly evolves  $\text{H}_2\text{S}$  when heated with concd. HCl but not on boiling with  $\text{PhO-NaOH}$  or  $\text{HgO}$ .  $\text{SP}(\text{OPh})_2\text{Cl}_2$ ,  $b_p$   $133$ - $5^\circ$ .  $\text{SP}(\text{OPh})_2\text{Cl}$ ,  $m$   $67^\circ$ . *Tri-p-tolyl thiophosphate*, obtained almost exclusively from  $\text{SPCl}_2$  and 4 mols. *p*-cresol refluxed in 25% NaOH,  $m$   $87^\circ$ , stable towards aq. alkalis and acids, hydrolyzed by boiling alc. KOH. *p-Tolylthiophosphoryl dichloride*,  $b_p$   $130$ - $40^\circ$ , and di-*p-tolylthiophosphoryl monochloride*,  $m$   $53^\circ$ , are obtained from 2.5 mols. *p*-cresol in a large excess of 10% NaOH shaken with 1 mol.  $\text{PSCl}_2$  until the odor of the  $\text{PSCl}_2$  disappears, both are exceedingly stable towards  $\text{H}_2\text{O}$  and alkalis, the monochloride being unchanged after refluxing 24 hrs. with 100 parts  $\text{H}_2\text{O}$ . Di-*Ph. p-tolyl thiophosphate*,  $\text{SP}(\text{OPh})_2\text{OC}_6\text{H}_4\text{Me}$ , from the dichloride and 3 mols.  $\text{PhONa}$  at  $180^\circ$ ,  $m$   $69^\circ$ . *Ph. di-p-tolyl ester*, obtained in the same way from the monochloride,  $m$   $54^\circ$ . Tri-*p-tolyl thionitriothiolphosphate*,  $\text{SP}(\text{SC}_6\text{H}_4\text{Me})_3$ , from 4 mols.  $\text{MeC}_6\text{H}_4\text{SH}$  in excess of 10% NaOH shaken with  $\text{SPCl}_2$ ,  $m$   $121.2^\circ$ . *Ph. thiophosphate anilide chloride*,  $m$   $153^\circ$ . I,  $m$   $155^\circ$ , mol. wt. in freezing  $\text{C}_6\text{H}_6$  353, easily sol. in dil. alkalis,  $\text{NH}_4\text{OH}$  and  $\text{Na}_2\text{CO}_3$ , and reprecip. by acids, Na salt. *Ph. phosphate dianilide*,  $m$   $126^\circ$ . II,  $m$   $165^\circ$ , mol. wt. in freezing  $\text{C}_6\text{H}_6$  524. *Ph. thiophosphate di-p-phenelide*,  $m$   $145^\circ$ , sol. in dil. NaOH and  $\text{Na}_2\text{CO}_3$ , and reprecip. by acids, loses  $\text{H}_2\text{S}$  from  $160^\circ$  up, titrates as a monobasic acid. Di-*Ph. disulfidodiphosphate di-p-phenelide*,  $m$   $153^\circ$ , mol. wt. in freezing  $\text{C}_6\text{H}_6$  612.

C. A. R.

Phosphorus-containing compounds and P-thiodiazophospholes. W. AUTENRIETH AND WILHELM MEYER. *Ber.* 58B, 848-51 (1925); cf. preceding abstr.—The chlorides  $\text{SP}(\text{OR})_2\text{Cl}_2$  and  $\text{OP}(\text{OR})_2\text{Cl}_2$  (or  $\text{OP}(\text{NHR})_2\text{Cl}_2$ ), where R = an aromatic group, react with bivalent N bases (*o*-diamines,  $(\text{CH}_2\text{NH}_2)_2$ ,  $\text{N}_2\text{H}_4$ ) with formation of cyclic compds. designated as P-thio- and P-oxodiazophospholes. Thus, *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$  fused with *p*- $\text{MeC}_6\text{H}_4\text{OPSCl}_2$  gives *p*-tolylxy-P-thiodihydrobenzodiazophospholium (*p*-tolyl

(thiophosphate *o*-phenylenediamide),  $\text{MeC}_6\text{H}_4\text{OPS}(\text{NH})_2\text{C}_6\text{H}_5$  (I); from  $\text{PhOPSCl}_2$  and  $(\text{CH}_3\text{NH}_2)_2\text{H}_2\text{O}$  in dil aq. soln. is obtained *phenoxy-P-thiodihydrodiazphospholium* (*Ph thiophosphate ethylenediamide*) (II);  $\text{N}_3\text{H}_4\text{H}_2\text{O}$  and  $(\text{PhO})_2\text{PSCl}$  give *di-Ph thiophosphate hydrazide* (III), with  $\text{PhOPSCl}_2$ ,  $\text{N}_3\text{H}_4\text{H}_2\text{O}$  yields, depending on the conditions,  $\text{SP}(\text{OPh})(\text{NHNH}_2)_2$  (IV) (Strecker and Heuser, *C. A.* 18, 3567), or the cyclic *P,P'*-diphenoxy-*P,P'*-dithioletrazadiphosphonium,  $\text{PhOPS}(\text{NH}:\text{NH})_2\text{PSOPh}$  (V). Heated in  $\text{C}_6\text{H}_6$ ,  $\text{PhOPSCl}_2$  and  $\text{o}$ - $\text{C}_6\text{H}_4(\text{NH}_2)_2$  give a *compd.* (VI) to which is provisionally assigned the structure  $\text{C}_6\text{H}_4(\text{N PSOPh})_2$ . A and Hildebrand's  $\text{PhOPS}(\text{NH})_2\text{C}_6\text{H}_5$  (*Ber.* 31, 1111(1908)), m  $185^\circ$ , has a mol. wt. in freezing  $\text{C}_6\text{H}_6$  of 241. I m.  $147^\circ$ , slowly dissolves in dil HCl and is recovered unchanged on evapn., is unchanged by cold aq. alkalis but on boiling decomps. with formation of a red-yellow soln. II m.  $189^\circ$ , is stable towards  $\text{H}_2\text{O}$ , aq. alkalis and dil acids. III m.  $63^\circ$ ; benzal deriv. m.  $129^\circ$ . V, from  $\text{PhOPSCl}_2$  and 2 mols.  $\text{N}_3\text{H}_4\text{H}_2\text{O}$  in 2 parts of a mixt. of equal parts of glycerol and  $\text{H}_2\text{O}$ , m  $183^\circ$ , mol. wt. in freezing  $\text{C}_{12}\text{H}_{22}$  412, forms no benzal deriv. IV, from  $\text{PhOPSCl}_2$  and 4 mols.  $\text{N}_3\text{H}_4\text{H}_2\text{O}$  in 2 vols. of the 1:1 glycerol- $\text{H}_2\text{O}$  mixt., m.  $95^\circ$ ; dibenzol deriv. m  $115^\circ$ . C. A. R.

The alkylmethylglycerols. RAYMOND DELABY AND GEORGES MOREL. *Compt. rend.* 180, 1408-10(1925).—Starting with vinylalkylcarbinols (I) the addn. of HOCl and sapon. gave only 12% yields of the methylalkylglycerols (II), but by addn. of Br to I, prepn. the di-Ac deriv. by KOAc and treating this with MeOH, the yields were for Me- $[\text{CH}(\text{OH})]_2\text{Me}$ ,  $b_{11}$  152-3°, 42%; Me- $[\text{CH}(\text{OH})]_2\text{Et}$ ,  $b_{11}$  155-6.5°, 38%; Me- $[\text{CH}(\text{OH})]_2\text{Pr}$ ,  $b_{11}$  162-4°, 31%. Applied to the prepn. of monoalkylglycerols the method gave yields of approx. 60%.

WM. B. PLUMMER

Examination of certain organic compounds by means of X-rays. J. J. THILLAT. *Rev. sci.* 63, 100-7(1925); cf. *C. A.* 19, 2150.—Brief review of Friedrich's, de Broglie's, Friedel's, Müller's and Shearer's work on mol. orientation in *faits, waxes, fatty acids* and *esters*, etc.

A. PAFINEAU-COUTURE

Chemical nature of the fats. I. The periodine number of fatty oils and unsaturated fatty acids. B. M. MARGOSCHES, LUDWIG FRIEDMANN AND WALTER TSCHÖRNER. *Ber.* 58B, 794-7(1925); cf. *C. A.* 18, 3434.—The object of the present work was to study the mechanism of the reaction between alc. I and fats after the double bonds have been satd. To 0.1-0.15 g. fat in 10 cc. of 99.8% alc. is added 20 cc. of 0.2 N alc. I, then 200 cc. of  $\text{H}_2\text{O}$  and at definite time intervals (up to 24 hrs.) the excess of I is titrated back and the III formed is detd. with  $\text{KIO}_3$ . Olive (I), castor (II) and linseed (III) oils and oleic (IV), ricinolic (V) and linolic (VI) acids were used. If the amts. of total I used and of I found as III, resp., are plotted against the times, the 2 curves run parallel after the unsatd. bonds have been satd., i. e., after the Hübl I no. has been reached (about 5 min.). The mechanism of the reaction is probably as follows: Part of the HI (50%) results from hydrolysis of the I ( $\text{I} + \text{H}_2\text{O} \rightarrow \text{HOI} + \text{HI}$ ); part of the HOI reacts with the fat ( $\text{RCH}:\text{CHR}' + \text{HOI} \rightarrow \text{RCHICH}(\text{OH})\text{R}'$ ) and the rest of the HI is formed according to the scheme  $\text{RCHICH}(\text{OH})\text{CH}_2\text{R}'' + \text{HOI} \rightarrow \text{RCHICH}(\text{OH})\text{CH}(\text{OH})\text{R}'' + \text{HI}$  (a), the velocity of this reaction varying from case to case. Besides the Hübl I no. (obtained in 5 min.), the value obtained after 24 hrs. and designated for short the periodine or P. I. no. is significant. Thus, while I and II have almost the same I nos., the P. I. no. of I is only about 33% and that of II almost 100% greater. Below are the I nos. after 5 min. and 24 hrs., resp. I 84.3, 119.7; II 87.7, 162.2; III 171.3, 225.1; IV 89.5, 107.0; V 90.0, 144.0; VI 192.8, 227.9. These results are sufficient to indicate that in the 24-hr. action of alc. I and  $\text{H}_2\text{O}$  on fats HO groups already present or formed during the reaction, as well as esterified  $\text{CO}_2\text{H}$  groups, have a special accelerating influence on reaction (a). C. A. R.

Labile nature of the halogen atom in organic compounds. XI. The halogenation of ethyl acetylsuccinate. ALEXANDER KILLEN MACHETH AND DAVID TRALL. *J. Chem. Soc.* 127, 1118-22(1925), cf. *C. A.* 19, 2027.—Et  $\alpha$ -chloroacetylsuccinate,  $b_{11}$  140-2°,  $n_D^{25}$  1.4420, from the ester and  $\text{SO}_2\text{Cl}_2$ ; it is quant. reduced by  $\text{N}_3\text{H}_4\text{H}_2\text{O}$ , giving Et 3-methyl-5-pyrazolone-4-acetate by the action of excess  $\text{N}_3\text{H}_4$  upon the reduction product. Excess  $\text{PhNHNH}_2$  gives Et  $\beta$ -carbethoxy- $\gamma$ -benzeneazo- $\Delta^8$ -pentenoate, lemon-yellow, m  $188^\circ$ . Hydrolysis gives an orange-yellow acid (probably  $\text{MeC}(\text{N}:\text{NPh})\text{CHCH}_2\text{CO}_2\text{H}$ ), m  $164-5^\circ$  (decompn). Et  $\alpha$ -bromoacetylsuccinate is obtained in good yield by bromination in aq. KOH, it  $b_{11}$  144-6°,  $n_D^{25}$  1.4600, 81% reaction occurs with  $\text{N}_3\text{H}_4\text{H}_2\text{O}$ .  $\text{PhNHNH}_2$  reacts with the Br ester but the only product isolated was  $\text{PhNHNH}_2\text{HBr}$ . Bromination by means of a rapid current of air gave 26% of the  $\alpha$ -Br ester, while Br in  $\text{CHCl}_3$  gave practically no  $\alpha$ -Br ester. Et chloromalonate,  $b_{11}$  127°, reacts with  $\text{N}_3\text{H}_4\text{H}_2\text{O}$ , without evolution of  $\text{N}_2$ , to give the hydrazide, m  $120^\circ$ .

and with  $\text{EtOH} \cdot \text{NH}_3$  to give the *ammonio deriv.*, *m.* 115°; with dil.  $\text{H}_2\text{SO}_4$ , the latter gives Et chloronitromalonate.

The formation of urea from ammonium bicarbonate solutions at (human) body temperature. FR. FICHTER AND WALTER KERN. *Helvetica Chim. Acta* 8, 301-6 (1925).—A soln. of 17.6 g.  $\text{NH}_4\text{HCO}_3$  in 50 cc.  $\text{H}_2\text{O}$ , plus 8.8 g. animal C as catalyst, was held at 37° for 14 days. The yield of urea (as the dioxanthyl deriv.) was 0.04 g. Royal Berlin porcelain ware was found to be the only available material which satisfactorily resisted the action of the  $\text{NH}_4\text{HCO}_3$ . At the end of the reaction period the solns. were evapd. in Pt vessels, the residue was dissolved in a little  $\text{H}_2\text{O}$  and pptd. with a soln. of xanthidrol in MeOH. Data are given covering the effect of various other (C and Pt) catalysts, of the  $\text{NH}_4\text{HCO}_3$  concn., etc.

WM. B. PLUMMER

Derivatives of semioxamazide. III. F. J. WILSON AND E. C. PICKERING. *J. Chem. Soc.* 127, 965-7 (1925); cf. C. A. 18, 2330.— $\text{H}_2\text{NCOCONHN} \cdot \text{CMePh}$ , heated 4 hrs. at 215°, gave  $(\text{N} \cdot \text{CMePh})_2$ ,  $(\text{NH}_2\text{CO})_2$ , cyclooxalylhydrazide (I) and acetophenone oxalylidihydrazone  $(\text{CONHN} \cdot \text{CMePh})_2$ , *m.* 250°.  $(\text{CONHN} \cdot \text{CMeCH}_2\text{CO}_2\text{Et})_2$  at 130-5° for 2 hrs. gives  $(\text{NH}_2\text{CO})_2$ , I and 3,4-dimethyl-1,2-pyrazo-6,7-pyrone, *m.* 247°. Dibenzyl ketone semioxamazone at 200° for 2 hrs. yields  $(\text{NH}_2\text{CO})_2$ , I and dibenzylketazine, *m.* 95-6°; the  $\text{Me}_3\text{CO}$  deriv., the same products and  $(\text{N} \cdot \text{CMe})_2$ ;  $\text{MeEtCO}$ , the same products and  $(\text{N} \cdot \text{CMeEt})_2$ . The intermediate oxalylidihydrazone were not isolated in these cases.

C. J. WEST

Reaction of levulose. O. ANGELUCCI. *Giorn. chim. ind. applicata* 6, 538 (1924).—Sugar, on oxidation with chromate mixt., gave appreciable amts. of HCHO. Comparative tests with glucose gave no HCHO, indicating that this was derived from the levulose of the sugar hydrolysis.

ROBERT S. POSMONTIER

Lactose. E. O. WHITTIER. *Chem. Reviews* 2, 85-125 (1925).—A review with 233 references.

C. J. WEST

Decarboxylation of polysaccharide acids; its application to the establishment of the constitution of pectins and to their determination. D. R. NANJI, F. J. PATON AND A. R. LING. *J. Soc. Chem. Ind.* 44, 253-8T (1925).—On oxidation of polysaccharides in alk. or neutral solns., when the linkage of the constituent units is other than 1,6, acids of the nature of conjugated glucuronic acid are formed; these are termed *uronic acids*. When these are heated with HCl for 4 hrs. under conditions similar to those employed for detg. pentoses, the yield of furfural is considerably less than the theory, but the  $\text{CO}_2$  evolved is nearly quant. Absorption of this by  $\text{Ba}(\text{OH})_2$  and titration of the excess is proposed as a method for detg. these compds. The following % of uronic acid anhydride were found by this method: agar-agar, 4.18; araban, 25.20; gum arabic, 16.24; gum tragacanth, 33.36; apple pectinogen, crude, 55.16; purified, 74.24; Ca pectate, 70.56; beet pectin, 72.32, 78.04; cytopectic acid (orange), 72.36; onion, 72.00;  $\alpha$ -orycellulose, 2.48;  $\beta$ -cellulose, 4.4;  $\gamma$ -cellulose, 2.63;  $\delta$ -cellulose, 5.44. The effect of pptn. of pectinogen preps. from alc. of varying concns. is shown by detg. the  $\text{CO}_2$  evolved and the Ca pectate pptd. The mode of occurrence of pectinogen in the plant and its possible constitution are discussed. Pectin material (pectinogen and pectic acid) may be calcd. from the  $\text{CO}_2$  evolved by the factor 5.66. The %  $\text{CO}_2$  evolved by various straws before and after extrn. with 0.5%  $(\text{CO}_2\text{H})_2$  is given; this corresponds principally with the amt. of pectin substances. There is no direct relationship either between the total pectin or the insol pectin and the tendency to lodging of crops.

C. J. W.

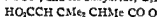
Unsaturated aldehydes and their relation to  $\alpha$ -lignin. ERIK HAGGLUND. *Cellulose-chemie* 6, 29-35 (1925).—Klason's hypothesis that  $\alpha$ -lignin contains an acrolein linkage is supported by H.'s work on the unsatd. aldehydes.  $\alpha$ -Lignosulfonic acid and  $\beta$ -sulfofropionaldehyde (and its derivs.) react very similarly with aromatic amines. In solns. that are sufficiently acid, these compds. form anils of the corresponding free  $\text{SO}_3\text{H}$  acids. In neutral soln. they form the normal amine salts of these acids. K.'s assumption that lignosulfonic acids tend to associate is also confirmed, since  $\text{PhCH} \cdot \text{CHCHO}$  has the property of condensing with itself (similar to the aldol condensation).  $\beta$ - $\text{H}_2\text{NC}_6\text{H}_4\text{H}_2$  reacts with acrolein to form  $\text{CH}_2 \cdot \text{CHCH} \cdot \text{NC}_6\text{H}_4\text{H}_2$ , *m.* 104°; with  $\text{MeCH} \cdot \text{CHCHO}$  to form  $\text{MeCH} \cdot \text{CHCH} \cdot \text{NC}_6\text{H}_4\text{H}_2$ , *m.* 140°; and with  $\text{PhCH} \cdot \text{CHCHO}$  to form  $\text{PhCH} \cdot \text{CHCH} \cdot \text{NC}_6\text{H}_4\text{H}_2$ , *m.* 120° (I). When treated in EtOH with HCl, I gives a compd. (II), probably  $\text{PhCH} \cdot \text{CHCH}(\text{OH})\text{C}(\text{CHPh})\text{CH} \cdot \text{NC}_6\text{H}_4\text{H}_2$ . HCl, yellow needles from alc., *m.* 218-20°, yellow leaflets from  $\text{CHCl}_3$  (contg. 0.5 mol.  $\text{CHCl}_3$ ). II is also formed when 2 g.  $\text{PhCH} \cdot \text{CHCHO}$  in 30 g. EtOH is treated with cold HCl gas, and subsequently with  $\beta$ - $\text{C}_6\text{H}_5\text{NH}_2$  in hot alc. II probably results from an aldol-like condensation.  $\beta$ - $\text{C}_6\text{H}_5\text{NH}_2$  derivs. of  $\beta$ -sulfoaldehydes were prepd. by the following general methods: the unsatd. aldehyde,  $\text{RCH} \cdot \text{CHCHO}$ , was treated with  $\text{NaHSO}_3$  (or with

HCl, followed by  $\text{Ag}_2\text{SO}_4$ ). With  $\text{NaHSO}_4$ , the resulting addn. product,  $\text{RCH}(\text{SO}_3\text{Na})\text{CH}_2\text{CH}(\text{OH})\text{SO}_3\text{Na}$  was then treated with 2 mols  $\beta\text{-C}_{10}\text{H}_7\text{NH}_2\text{HCl}$  with the formation of a naphthylammonium naphthylsulfonate of the type  $\text{RCH}(\text{SO}_3\text{NH}_2\text{C}_{10}\text{H}_7)\text{CH}_2\text{CH}(\text{OH})\text{NC}_{10}\text{H}_7$ , which on acid hydrolysis is split to the free naphthylsulfonic acid  $\text{RCH}(\text{SO}_3\text{H})\text{CH}_2\text{CH}(\text{OH})\text{NC}_{10}\text{H}_7$  and  $\beta\text{-C}_{10}\text{H}_7\text{NH}_2\text{HCl}$ . By the use of these methods the following new compds were prepd:  $\beta$ -Naphthylammonium- $\gamma$ -[ $\beta$ -naphthylamino]propylsulfonate,  $\text{C}_{10}\text{H}_7\text{NCHCH}_2\text{CH}_2\text{SO}_3\text{NH}_2\text{C}_{10}\text{H}_7$ , readily converted to the free acid, reddish brown, m 125-6°,  $\beta$ -naphthylammonium  $\gamma$ -[ $\beta$ -naphthylamino]- $\alpha$ -methyl propylsulfonate, the corresponding free acid, dark brown, m 251°;  $\beta$ -naphthylammonium  $\gamma$ -[ $\beta$ -naphthylamino]- $\alpha$ -phenylpropylsulfonate(?), decomps on attempted recrystn. from  $\text{H}_2\text{O}$ , free acid, brown, m 198-9°, whose  $\text{NH}_4$  salt m 85°.  $\text{NaO}_2\text{SCHPhCH}_2\text{CH}(\text{OH})\text{SO}_3\text{Na}$ , when treated with  $\text{HONH}_2\text{HCl}$  followed by  $\beta\text{-C}_{10}\text{H}_7\text{NH}_2\text{HCl}$ , yielded  $\beta$ -naphthylammonium  $\gamma$ -oximino- $\alpha$ -phenylsulfonate, pink ppt. Lignosulfonic acids prepd by neutralizing com. or laboratory samples of sulfite liquor with  $\text{CaCO}_3$  and  $\text{Ca}(\text{OH})_2$ , followed by pptn. with  $\text{NaCl}$  and treatment with  $\text{HCl}$ , when dissolved in  $\text{H}_2\text{O}$  and treated with  $\beta\text{-C}_{10}\text{H}_7\text{NH}_2\text{HCl}$  gave ppts., the properties of which essentially confirmed the work of Klason. The N/S ratio was approx 1:1 in all cases (2.2-2.4% N, and 5.2-5.6% S). Similarly other derivs. prepd by K. from sulfite liquor were reproduced by H. The question as to whether lignosulfonic acid forms a cyclic  $\beta\text{-C}_{10}\text{H}_7\text{NH}_2$  deriv., of the type suggested by K. is left open by H., who states that it is more probable that the  $\text{SO}_3\text{H}$  group enters the  $\beta$ -position with respect to the C at carrying the aldehyde group, rather than the  $\alpha$ -position as suggested by K. Cross and Engelstad's method for delignifying wood at 107° with  $\text{H}_2\text{SO}_4$  (C. A. 18, 3054), and treatment of the undialyzed sulfite liquor with  $\beta\text{-C}_{10}\text{H}_7\text{NH}_2\text{HCl}$  yielded an  $\alpha$ -lignosulfonate deriv., amounting to approx. 60% of the total lignin. The  $\alpha\text{-C}_{10}\text{H}_7\text{NH}_2$  deriv. contains 4.17-4.3% N and about 4.3% S (N/S ratio = 2.04). If the  $\beta\text{-C}_{10}\text{H}_7\text{NH}_2$  pptn. is made in very dil. soln. of the sulfite liquor, the resulting ppt. is relatively higher in S and lower in N, indicating hydrolysis to the free  $\text{SO}_3\text{H}$  acid. The Cross-Engelstad sulfite liquor, when treated with  $\alpha\text{-MeC}_6\text{H}_4\text{NH}_2\text{HCl}$ , gave a ppt. contg. 3.2% N;  $\alpha$ -toluidine is split off when this substance is titrated with  $\text{NaOH}$ , indicating the presence of an  $\text{NH}_2$ -like salt in the original ppt., as well as a partial association of the lignosulfonic acid. The same sulfite liquor, when treated with  $\alpha\text{-C}_{10}\text{H}_7\text{NH}_2$ , yielded products which varied with the intensity of the acidity of soln. The more strongly acid the soln., the lower the N content of the ppt. H. finds no expl. evidence that the lignosulfonic acids obtained by the usual sulfite process and by the Cross-Engelstad process represent different lignin fractions. L. E. Wise

**Humic acids.** VII. Several properties and reactions of the humic acids and humins. WILHELM ELLER *Ann.* 442, 160-80 (1925); cf. C. A. 17, 2269.—Melting various humins with  $\text{KOH}$  at 230-60° gives products with a much higher C content than that of the original materials, a natural humin with C, 60.21; H, 3.42; N, 1.85; S, 1.42; ash, 1.52 gave a product with C, 70.61; H, 3.74; N, 1.69; S, 0.74; ash, 1.26. Values are also given for an impure and a pure hydroquinol humic acid, a N-contg. product and an impure carbohydrate humic acid. Since the total N is not removed, this disproves Hoppe-Seyler's contention that the N is entirely eliminated as  $\text{NH}_3$  and favors the idea that the N is that of constitution and not adsorbed. Humic acids prepd from  $\text{H}_2\text{N}\text{-C}_6\text{H}_4\text{OH}$  vary in compn., depending upon the oxidizing agent used and the concn. of the alkali. Those from the  $p$ -deriv. contained 52.6-60.4% C, 3.2-4.8% H, 4.7-7.6% N; from the  $\alpha$ -deriv., 53.2-60.2 C, 3.2-4.3 H, 5.1-7.4 N, those from the  $m$ -deriv., 48.2-53.4 C, 2.9-3.4 H, 4.6-5.7 N. In general they show the properties of the humic acids prepd from phenols. Hydroquinol, oxidized with  $\text{K}_2\text{S}_2\text{O}_8$  in 24%  $\text{NH}_4\text{OH}$ , gives products with 55.4-58.5 C, 3.3-3.4 H and 10.2-10.9 N. Synthetic humic acids, dissolved in  $\text{NH}_4\text{OH}$  and pptd. with  $\text{HCl}$ , show an increase in N content, natural humic acids do not. Dialysis of an acid from  $p\text{-H}_2\text{NC}_6\text{H}_4\text{OH}$  showed no decrease in N content. Distn. of humic acids with 1:1 alkali splits off only a part of the N, those from aminophenols lose 8-9%, from hydroquinol contg. 10.2-10.9% N, 13-26% and from those contg. 1.6-2.4%, 30-32%. Reduction of humic acids with  $\text{HI}$  and red P gives an  $\text{Et}_2\text{O}$ -sol. fraction, which consists of a hydrocarbon mixt. and an acid fraction. The former is a mixt. of liquid and solid fractions. The liquid products contain 88.19-88.68% C, 11.41-11.82% H and have a mol. wt. of 211-261. The solid products contain 88.06-88.40% C, 11.71-11.84% H and have a mol. wt. of 671-702. The av. ratio of C:H is 1:1.58. These values are very similar to those for the products from lignin, cellulose and glucose. Upon dry distn., decompn. becomes marked at 230°, a liquid distillate and a non-combustible gas being formed. Between 450-500° a combustible gas is formed. The following figures give the % of distn. residue, the volatile distillate ( $\text{H}_2\text{O}$ , tar) and gas and loss. natural humic acid, 51.9, 23.4 (21.8, 1.8), 24.7; hydroquinol-

humic acid, 40.2, 43.1 (42.9, 0.2), 16.7; carbohydrate humic acid, 59.2, 20.6 (20.2, 0.4), 20.2. The 1st 2 distillates are acid, the 3rd basic. C. J. WEST

Ring-chain tautomerism. XIII. Three-carbon ring-chain tautomerism in a bridged ring system. J. W. BAKER *J. Chem. Soc.* 127, 985-90 (1925), cf. C. A. 19, 1697. —Et 1,2-dibromocyclohexane-1-acetate (from 20 g each of Br and Et cyclohexeneacetate in  $\text{CHCl}_3$ ) condenses with 1 mol  $\text{CHNa}(\text{CO}_2\text{Et})_2$  to give Et 2-bromo- $\Delta^1$ -cyclohexeneacetate (I),  $b_p$  125–35°, which condenses with a 2nd mol  $\text{CHNa}(\text{CO}_2\text{Et})_2$  to give Et  $\Delta^1$ -cyclohexene-1-acetate-2-malonate (II),  $b_p$  210°. Hydrolysis with EtOH-KOH gives the free acid (III),  $m$  210°, hydrolysis with 20% HCl yields 2-carboxycyclohexane-1,2-diacetic acid,  $m$  186°, which does not decolorize Br or alk.  $\text{KMnO}_4$ , this also results by heating I with 20% HCl for 24 hrs. Oxidation of III with alk.  $\text{KMnO}_4$  gives 1,2-dihydroxycyclohexane-1,2-diacetic acid lactone,  $m$  187°. The ozonide of II upon hydrolysis gave no fission products, the lactone being the only product identified. Heating III at 215° for 15 min gives  $\Delta^1$ -cyclohexene 1,2-diacetic acid,  $m$  122°. These results can be explained only by the existence, in the parent ester, of a tautomeric equilibrium such as was previously postulated between open-chain and bicyclic forms. In the titration of the ester with Br no clear line of demarcation between rapid and slower absorption of Br could be observed, either the re-establishment of the equilibrium is too rapid for detection by this method or the equilibrium is largely displaced in favor of the unsaturated form. In the latter case the formation of the saturated acid to the extent of 34% can be accomplished only by the conversion of a large quantity of the unsaturated ester into its saturated, bicyclic form, this is considered as establishing the existence of ring-chain tautomerism of the 3-C type. XIV. The structure of Balbiano's acid. EUGENE ROYSTEIN, ARNOLD STEVENSON and J. F. THORPE *Ibid.* 1072-80. —The lactic acid,  $m$  163° (I), obtained by Balbiano by the reduction of the acid,  $m$  120°, is not identical with Blanc's synthetic lactic acid,  $m$  165.5–6° (II) (cf. *Bull. soc. chim.* 25, 68 (1901)). Di-Et  $\alpha$ -keto- $\beta,\beta$ -dimethylpentane- $\alpha,\gamma$ -dicarboxylate,  $b_p$  148–9° (75% yield),  $\text{BrCH}_2\text{CO}_2\text{Et}$  and Zn in  $\text{C}_6\text{H}_6$  give, with this ester, the  $\gamma$ -lactone of  $\delta,\delta$ -dicarboethoxy- $\beta$ -hydroxy- $\gamma,\gamma$ -dimethylpentane- $\gamma$ -carboxylic acid,  $b_p$  190–220°, obtained as needles,  $m$  86°, and minute prisms,  $m$  115° ( $m$  p of mixt., 75°), hydrolysis of the higher melting form with KOH gives two acids,  $\text{C}_8\text{H}_{14}\text{O}_4$ ,  $m$  178° and 140° (decompn.), the lower melting form gives only the acid  $m$  178°; with 10% HCl, only 1 mol. of EtOH is eliminated, giving, from the higher melting form, an acid  $\text{C}_8\text{H}_{14}\text{O}_4$ ,  $m$  123° (decompn.), from the lower melting form,  $m$  146°. Ethyl methoxycarboxylate,  $b_p$  120°; HBr, followed by esterification, gave Et  $\alpha$ -keto- $\beta,\beta$ -diethylglutarate,  $b_p$  140–1°, which with  $\text{BrCH}_2\text{CO}_2\text{Et}$  and Zn gave the lactone of  $\gamma$ ,  $\delta$ -dicarboethoxy- $\gamma$ -hydroxy- $\beta,\beta$ -dimethylbutane- $\alpha$ -carboxylic acid,  $m$  54°,  $b_p$  199–204°, hydrolysis of the lactone with EtOH-NaOH gives an acid,  $\text{C}_8\text{H}_{14}\text{O}_4$ ,  $m$  54°, and its anhydride,  $\text{C}_8\text{H}_{10}\text{O}_5$ ,  $m$  126–8°.



(I)



(II)

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Interaction of thiocyanogen with unsaturated compounds. FREDERICK CHALLENGER and T. H. BOTT, *J. Chem. Soc.* 127, 1039-42 (1925). —The compd. from  $\text{PhCH:CHAc}$  and  $\text{SCN}$  (cf. C. A. 17, 2564) is  $\alpha$ -thiocyanostyryl Me ketone,  $m$  119°, mol. wt. in freezing  $\text{C}_6\text{H}_6$ , 185, dibromide,  $m$  138° (decompn.). Oxidation with 4%  $\text{KMnO}_4$  gave  $\text{K}_2\text{SO}_4$ ,  $\text{BzOH}$  and traces of a fatty acid. Br in KOH gave  $\text{PhCH:CHCO}_2\text{H}$ . Reduction gave  $\text{PhCH}_2\text{CH}_2\text{Ac}$  and a trace of a solid,  $m$  157°. Distyryl ketone and excess  $\text{SCN}$  give the compd.  $\text{C}_{14}\text{H}_{17}\text{O}_2\text{NS}_2$ ,  $m$  151°, the comd.  $\text{H}_2\text{SO}_4$  soln is deep blue. Carvone and  $\text{SCN}$  give the compd.  $\text{C}_{11}\text{H}_{15}\text{ONS}$ ,  $m$  254°.

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Polyaryl-substituted vinylcarbinols and their derivatives. VI. True derivatives of diphenylstyrylmethane. K. ZIEGLER, K. RICHTER and B. SCHNELL, *Ann.* 443, 161-80 (1925); cf. C. A. 19, 1566. —1,1,3-Triphenyl-1,2-dibromopropane (I),  $m$  94–5°, in 94% yield from the corresponding propene and Br, heated a few degrees above its  $m$  p., it splits off HBr, giving  $\text{Ph}_2\text{C}(\text{Br})\text{CH}_2\text{Ph}$  (II),  $m$  97–8°. I and boiling MeOH give 1,1,3-triphenyl-2-bromo-1-methoxypropane,  $m$  84–5°; warming with AcOH contg. a trace of mineral acid or satg. an EtOH soln with HCl or HBr gives II.  $\text{AgONa}$  gives diphenylstyryl Me ether (III),  $b_p$  187°,  $m$  78–9° (90% yield); this is identical with the isomer described by Straus and Ehrenstein (C. A. 19, 1410). No trace of their high-melting isomer was found. MeONa and  $\text{Ph}_2\text{C}(\text{CH}_3)\text{CHClPh}$  give principally the ether,  $m$  97–8°, and only a small amt. of III;  $\text{Ph}_2\text{C}(\text{OH})\text{CH}(\text{CH}_3)\text{Ph}$  and K in PhMe, with MeI, give only III. III may be rearranged to the higher melting isomer by adding a trace of MeOH- $\text{H}_2\text{SO}_4$  to the alc. soln. III, oxidized with  $\text{KMnO}_4$  in AcMe, gives

BzOH and  $\text{Ph}_2\text{C}(\text{OH})\text{CO}_2\text{H}$ . Reduction of III gives 1,1,3-triphenylpropyl Me ether, m. 111–2°. Bromostyrene, Mg and  $\text{Ph}_2\text{CO}$  give about 20% of diphenylstyryl carbinol, m. 109.5–10.5°; it may be distd. at 0.2 mm. With  $\text{MeOH-H}_2\text{SO}_4$  it gives the Me ether, m. 97–8°. Either the carbinol or its Me ether, with HCl, gives  $\text{Ph}_2\text{C:CHCH}_2\text{CIPh}$ , m. 94–5°. With concd.  $\text{H}_2\text{SO}_4$  at –20°, either gives 1,3-diphenylindene. Diphenylstyrylmethane,  $b_{\text{D}}^{20}$  230°,  $b_{\text{D}}^{25}$  180°, m. 97–8°. Reduction gives  $\text{Ph}_2\text{CCH}_2\text{CH}_2\text{Ph}$ ; oxidation gives BzOH and  $\text{Ph}_2\text{CHCO}_2\text{H}$ . C. J. WEST

Polarization of nitrosobenzene. R. ROBINSON. *Chemistry & Industry* 44, 456–8 (1925).—A "crotonoid system" comprises a group such as CO in association with an unsatd. center. A "crotonoid system" comprises an atom of an element capable of rising to a higher valency, directly attached to an unsatd. system such as an ethylenic linkage or an aromatic nucleus.  $\text{PhNO}$  contains overlapping crotonoid and crotenoid systems, and therefore induces addn. of + and – ions to the *o*- and *p*-positions, and never to the *m*-position. T. S. CARSWELL

Mercuriation of aromatic substances. I. Toluene. SAMUEL COFFEY. *J. Chem. Soc.* 127, 1029–32 (1925).— $\text{PhMe}$ ,  $b_{\text{D}}^{20}$  109.4°, was heated with 0.2 part of  $\text{Hg}(\text{OAc})_2$  for 5–6 hrs., the insol. polymercurated  $\text{PhMe}$  was washed with  $\text{PhMe}$  and a little  $\text{AcOH}$ , the soln. and washings were distd. up to 120°, the residue was poured into  $\text{KBr}$  soln., the bromo-mercuritoluenes were converted into  $\text{BrC}_6\text{H}_4\text{Me}$  and oxidized to  $\text{BrC}_6\text{H}_4\text{CO}_2\text{H}$ , a sepn. of which indicated the ratio of *o*:*m*:*p*-derivs. to be 43:13:44. A method for the sepn. of  $\text{BrC}_6\text{H}_4\text{CO}_2\text{H}$  is indicated. C. J. WEST

Reply to Mr. Hans Lecher (valence problem of sulfur). WILHELM STEINHOFF. *Ber.* 58B, 785 (1925).—See L. C. A. 19, 1855. C. A. R.

Phosphorus chloronitrides. H. ROSSET. *Bull. soc. chim.* 37, 518–22 (1925).—See C. A. 19, 1699. M. HEIDELBERGER

1,2-Diamino-4,5-*o*-quinone and some derivatives. ERNST HORN. *Helvetica Chim. Acta* 8, 275–80 (1925).—By complete acetylation of 4-aminopyrocatechol (I) and treatment with  $\text{HNO}_3$  is obtained 80% of 4-acetamino-5-nitrosopyrocatechol, which with  $\text{SnCl}_2$  in alc. gives 50% of 4,5-diaminopyrocatechol (II). On addn. of a slight excess  $\text{NH}_3$  to aq.  $\text{HCl}$  and shaking with air, 1,2-diamino-4,5-*o*-quinone (III), is obtained as a brown ppt., not sol. enough in available solvents to be recrystd.; in  $\text{NaOH}$  it is pure red, in concd.  $\text{H}_2\text{SO}_4$  pure violet becoming orange on diln. On warming with dil.  $\text{H}_2\text{SO}_4$ , III yields dihydroxyquinone. By boiling  $\text{HCl}$  with  $\text{Ac}_2\text{O}$  plus the theoretical amt.  $\text{NaOAc}$ , its tetra-Ac deriv., m. 224–5°, is obtained. Diaminoquinone anil, m. 207.5°, is obtained from the mono-Ac deriv. of I by  $\text{PhNH}_2$  in alc. at 50°. With *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2\text{HCl}$ , in alc. plus a little  $\text{HCl}$ , III gives 40% of 2,3-phenolsulfanilic acid (the 4th known isomer), pptd. as the  $\text{HNO}_3$  salt; the latter and the  $\text{HClO}_4$  salt are orange, the chloroplatinate is reddish brown. In  $\text{H}_2\text{SO}_4$  it gives 4 series of salts, viz., in fuming acid brownish red, in 98% acid olive-green becoming brown on slight diln. and orange (with fluorescence) after much  $\text{H}_2\text{O}$  is added. WM B. PLUMMER

Dependence of rotatory power on chemical constitution. XXV. Three optically active alcohols containing a phenyl group and some esters derived therefrom. L. F. HEWITT AND JOSEPH KENYON. *J. Chem. Soc.* 127, 1094–104 (1925); cf. C. A. 19, 1407.—One of the most pronounced differences between an optically active alc. contg. a Ph group and the corresponding aliphatic alc. contg. the same no. of C atoms is that the rotatory power of the former class is much greater than that of the latter; the further the Ph group is removed from the asymt. C atom, the smaller becomes its enhancing effect on the rotatory power. The values of the rotatory dispersion  $\alpha_{\text{D}}^{25}/\alpha_{\text{D}}^{55}$  for the members of the aliphatic series of alcs. are almost const., lying between 1.53 and 1.68, while the corresponding values for the members of the aromatic series of alcs. vary between 1.53 and 1.83. The rotatory dispersions of the former class of compds. are only slightly affected by changes in temp., while those of the latter are very susceptible to this influence. These aromatic alcs. show complex rotatory dispersion, since their rotatory powers cannot be expressed by a Drude equation of 1 term. The values of the rotatory dispersion of the esters of these alcs. lie between 1.78 and 2.51. *dl*- $\beta$ -Phenylethylethylcarbinyl II phthalate m. 74°. The strychnine salt, *l*-B, *d*-A, m. 158°,  $[\alpha]_{\text{D}}^{25}$  –38.7° (c, 5% in  $\text{CHCl}_3$ ), is obtained pure after 6 crystals from  $\text{MeOH-Me}_2\text{CO}$ ; the mother liquors gave a cinchonidine salt, *l*-B, *l*-A, m. 154°,  $[\alpha]_{\text{D}}^{25}$  –54.2° (c, 5% in  $\text{EtOH}$ ). The *d*- and *l*-II phthalates form viscous gums,  $[\alpha]_{\text{D}}^{25}$  = 42.9° (c, 5% in  $\text{EtOH}$ ). The *d*-(I) and *l*- $\beta$ -phenylethylethyl carbinols (II), m. 38°,  $b_{\text{D}}^{20}$  143°. *dl*- $\beta$ -Phenylethylpropylcarbinyl II phthalate, m. 108°; the brucine salt, *l*-B, *l*-A, m. 95°,  $[\alpha]_{\text{D}}^{25}$  –2.1° (c, 5% in  $\text{EtOH}$ ), brucine salt, *l*-B, *d*-A, m. 75°,  $[\alpha]_{\text{D}}^{25}$  –12.5°. The *l*-(III) and *d*-H phthalates

m. 75° and have  $[\alpha]_{D}^{25} = 25.5^\circ$ . *d*-(IV) and *l*-Phenylethylpropylcarbinols (V),  $b_{11}$  146°, m. 34°, and are volatile in steam. *dl*-Phenyl- $\beta$ -phenylethylcarbinol ( $\alpha$ , $\beta$ -*diphenyl- $\alpha$  propanol*), m. 45.5°,  $b_{11}$  200°; the *H* phthalate, m. 110°; *brucine salt*, *l*-B, *l*-A, m. 121° ( $[\alpha]_{D}^{25} -8.8^\circ$  (c, 5% in EtOH); *strychnine salt*, *l*-B, *d*-A, m. 189°. The *d*- and *l*-H phthalates (VI), viscous gums, with  $[\alpha]_{D}^{25} = 8.9^\circ$ . *d*-(VII) and *l*-phenyl- $\beta$ -phenylethylcarbinols (VIII),  $b_{11}$  195°, m. 54°. I,  $d_{11}^{20}$  0.9687,  $d_{11}^{40}$  0.8773 (values also given for 46.3°, 72.5°, 100.5° and 131.5°);  $[\alpha]_{D}^{25}$  18.95°, 23.00° and 38.98°,  $[\alpha]_{D}^{40}$  18.70°, 23.30° and 39.98° where  $\lambda = 5893, 5461$  and 4358 (values are also given for other temps. and for solns. in  $C_6H_6$ , EtOH and  $CS_2$ ). *I formate*,  $b_{11}$  135°,  $d_{11}^{20}$  0.9980,  $d_{11}^{40}$  0.8980 ( $[M]_{\lambda}$  for this and other esters are given for  $\lambda = 6708, 5893, 5780, 5461, 4358$ ). *I acetate*,  $b_{11}$  147°,  $d_{11}^{20}$  0.9829,  $d_{11}^{40}$  0.8825. *II propionate*,  $b_{11}$  150°,  $d_{11}^{20}$  0.9731,  $d_{11}^{40}$  0.8703. *V formate*,  $b_{11}$  147°,  $d_{11}^{20}$  0.9872,  $d_{11}^{40}$  0.8959. *V acetate*,  $b_{11}$  154°,  $d_{11}^{20}$  0.9725,  $d_{11}^{40}$  0.8750. *IV propionate*,  $b_{11}$  163°,  $d_{11}^{20}$  0.9629,  $d_{11}^{40}$  0.8688. *VII formate*,  $b_{11}$  195°,  $d_{11}^{20}$  1.0790,  $d_{11}^{40}$  0.9741. *VII acetate*,  $b_{11}$  165°,  $d_{11}^{20}$  1.0670,  $d_{11}^{40}$  0.9672. The sp rotatory powers of IV, VII, I, III and VI at room temp. in various solvents are reported; also, the refractive index of V and of the above esters at 20° for a no. of wave lengths. The observed rotatory powers for the alcs. and esters in the homogeneous state of a 50 mm layer of liquid are reported for a no. of wave lengths and various temps from 20° to 140°. *d*- $\beta$ -Phenylethylmethylcarbinyl formate,  $b_{11}$  120°,  $d_{11}^{20}$  1.0083,  $d_{11}^{40}$  0.9119; *acetate*,  $b_{11}$  130°,  $d_{11}^{20}$  0.9854,  $d_{11}^{40}$  0.8860; *propionate*,  $b_{11}$  141°,  $d_{11}^{20}$  0.0790,  $d_{11}^{40}$  0.8792.  $[M]_{\lambda}$  for these esters is given for the above named 5 wave lengths. XXVI. Four alcohols containing the vinyl group and some esters derived therefrom. J. KENYON AND D. R. SNELLGROVE. *Ibid* 1169-81.—Comparison of the satd. and unsatd. optically active alcs. shows that the presence of the double bond exalts the rotatory power to a very considerable extent; in the case of the H phthalates, the exalting effect of unsatn. becomes much less pronounced. The alcs. possess simple rotatory dispersion within the exptl range and equations are given for the 4 alcs.; unsatn. increases  $\lambda_D$ , bringing it nearer the visible region; with increasing mol. wt.,  $\lambda_D$  increases in the "vinyl" series and diminishes in the "Et" series. The double bond also has an exalting influence on the refractive index. The unsatd. alc. has the higher density. All esters prepd. exhibit complex rotatory dispersion. *dl*-Methylvinylcarbinyl *H* phthalate, m. 5°; *d*-deriv., m. 52-3°,  $[\alpha]_D^{25}$  40.5° (c, 5% in EtOH); *l*-deriv., m. 52-3°,  $[\alpha]_D^{25} -40.6^\circ$  (5% in EtOH). This was resolved by *brucine*, the *d*-salt, m. 120-2°. *dl*-Ethylvinylcarbinyl *H* phthalate, oil, as are the *d*- and *l*-series. The *d*-strychnine salt, m. 159-60°, gave a *d*-H phthalate with  $[\alpha]_D^{25}$  26.2° (c, 5% in EtOH); *dl*-Propylvinylcarbinyl *H* phthalate, m. 62-3°. The *l*-strychnine salt, m. 170-2°, gave a *l*-H phthalate, m. 58-60° ( $[\alpha]_D^{25} -16.05^\circ$  (c, 5% in EtOH); its *brucine salt*, m. 118-20°. *dl*-Butylvinylcarbinyl *H* phthalate, m. 56-7°; *l*-strychnine salt, m. 174-6°; *d*-morphine salt, m. 114-6°. The *d*- and *l*-H phthalates, m. 50-2° and have  $[\alpha]_D^{25} = 12.6^\circ$  (c, 5% in EtOH). *d*-Methylvinylcarbinol,  $d_4$  0.8362, 0.8156, 0.7979 and 0.7746 at 15.5°, 39°, 59.5° and 84°. Refractive indexes for this and the alcs. and esters are given at 20° for 13 wave lengths; the rotatory powers are given at various wave lengths for various temps. *d*-Ethylvinylcarbinol,  $d_4$  0.8404, 0.8200, 0.8021, 0.7890 and 0.7764 at 20.5°, 42.8°, 60.8°, 76.2° and 88.2°; *formate*,  $b_{11}$  115.5-6.5°,  $d_{11}^{25.5}$  0.8902; *acetate*,  $b_{11}$  126.5-7.5°,  $d_{11}^{21.1}$  0.8805. *l*-Propylvinylcarbinol,  $d_4$  0.8403, 0.8186, 0.7928, 0.7656, 0.7432 at 15°, 42°, 68.5°, 94° and 120°. *d*-Butylvinylcarbinol,  $d_4$  0.8345, 0.8144, 0.7918, 0.7628 and 0.7528 at 22.8°, 49°, 73.5°, 110° and 121°; *formate*,  $b_{11}$  155-7°,  $d_{11}^{20}$  0.8754; *acetate*,  $b_{11}$  165-7°,  $d_{11}^{20}$  0.8682; *butyrate*,  $b_{11}$  198-200°,  $d_{11}^{20}$  0.8696; *benzoate*,  $b_{11}$  152-3°,  $d_{11}^{20}$  1.0033. Reduction of *l*-butylvinylcarbinol, with  $[\alpha]_D^{25} -25^\circ$ , gave a *l*-butylethylcarbinol, with  $[\alpha]_D^{25} -8.11^\circ$  and identical in all its properties with that obtained by the resolution of the *dl*-compd. Reduction of the acetate and hydrolysis also gave the same product.

C. J. WEST

Nitration of the carbonate and ethyl carbonate of *m*-hydroxybenzaldehyde. F. A. MASON AND H. JENKINSON. *J. Chem. Soc.* 127, 1193-9 (1925).—*m*-Aldehydophenyl carbonate, m. 132-4°, results in 90% yield by passing  $COCl_2$  into *m*-HOC<sub>6</sub>H<sub>4</sub>CHO in a mixt. of NaOH, Na<sub>2</sub>CO<sub>3</sub> and NaCl. Nitration gives 97% of the nitro-carbonate, m. 194-8°, which, on hydrolysis, gives 95% 6,3-O<sub>2</sub>N(HO)C<sub>6</sub>H<sub>4</sub>CHO, m. 167°. *m*-Aldehydophenyl Et carbonate,  $b_{11}$  165-7°,  $b_{11}$  289-92°,  $d_4$  1.42, yield, 95%. Nitration gives 95% of a mixt., which, on hydrolysis, gives 41% of 6,3-O<sub>2</sub>N(HO)C<sub>6</sub>H<sub>4</sub>CHO. The aldehyde yields a *tri-Ac deriv.*, m. 120°; the *Bz deriv.*, m. 104-5°; the *phenylhydrazone*, red, m. 185-95°; the Na salt is deep red and m. above 270°; *oxime*, pale yellow, m.

179-80° and gives an orange-red Na salt; semicarbazone, pale yellow, decomp. 245-60° and gives an orange Na salt. C. J. WEST

Compounds formed by the action of bromine upon benzaldehyde phenylhydrazone. F. D. CHATTAWAY AND A. J. WALKER. *J. Chem. Soc.* 127, 975-84 (1925). Cf. Cusa and Vecchiotti, *C. A.* 10, 2893 —  $\text{PhCH} \cdot \text{NNHPh}$  and 3 mols Br in AcOH give  $\omega$ -bromobenzaldehyde 2,4-dibromophenylhydrazone (I), m 114°, whose structure is confirmed by its synthesis from 2,4- $\text{Br}_2\text{C}_6\text{H}_3\text{NHNHBr}$  and  $\text{PBz}$ . The constitution suggested by C and V has been disproved by the synthesis of *p*-bromobenzaldehyde 2,4-dibromophenylhydrazone, m 126°. I and AcONa in AcOH give  $\alpha$ -acetyl- $\beta$ -benzoyl-2,4-dibromophenylhydrazine, m 158-9°, also obtained by the successive action of  $\text{BzCl}$  and  $\text{AcCl}$  upon 2,4- $\text{Br}_2\text{C}_6\text{H}_3\text{NHNH}_2$ . Hydrolysis gave 2,4- $\text{Br}_2\text{C}_6\text{H}_3\text{NHNH}_2$ ,  $\text{BzOH}$  and  $\text{AcOH}$  I and concd  $\text{NH}_4\text{OH}$  give benzaldehyde 2,4-dibromophenylhydrazidine,  $\text{Br}_2\text{C}_6\text{H}_3\text{NHN}:\text{CPhNH}_2$ , m 115° ( $\text{HCl}$  salt, m 260° (decompn)), also obtained by the action of  $\text{NH}_3$  upon  $\omega$ -chlorobenzaldehyde 2,4-dibromophenylhydrazone, m 109°. KCN and I in dil EtOH give the  $\omega$ -CN deriv., m 139°, which exists as long, pale yellow hair like crystals and somewhat deeper yellow stout crystals, the transformation in EtOH requiring about 2 days. I and  $\text{PhNHNH}_2$  in EtOH give dibromomazobenzene,  $\text{Br}_2\text{C}_6\text{H}_3\text{NHN}:\text{N CPhN NPh}$ , reddish brown, m 173-4°.  $\text{PhCH} \cdot \text{NNHPh}$ , brominated in AcOH-AcONa, gives 50% of 1,4-di-*p*-bromophenyl-3,6-diphenyl-1,4-dihydro-1,2,4,5-tetrazine,  $\text{PhC N N(C}_6\text{H}_4\text{Br) CPh N NC}_6\text{H}_4\text{Br}$  (II), yellow, m 265°; mol wt. in freezing  $\text{C}_6\text{H}_6$ .

535, sol in concd  $\text{H}_2\text{SO}_4$  with a yellow color, changed to deep blue by an oxidizing agent, reduction gives  $p\text{-BrC}_6\text{H}_4\text{NH}_2$ ; heated above its m p, it yields  $\text{PhCN}$ , which also results upon distn with Zn dust. II was also obtained from 4- $\text{BrC}_6\text{H}_4\text{NHN CHPh}$  and Br in AcOH-AcONa and in 90% yield from  $\text{PhNHN}:\text{CClPh}$  2,4- $\text{Br}_2\text{C}_6\text{H}_3\text{NHN CHPh}$  and 2 mols Br in AcOH-AcONa give principally I but also a small amt of 1,4-di[2,4-dibromophenyl]-3,6-diphenyl-1,4-dihydro-1,2,4,5-tetrazine (III), pale yellow, m 255°, mol wt in boiling  $\text{CHCl}_3$ , 874; the yellow concd  $\text{H}_2\text{SO}_4$  is turned deep blue on addn of an oxidizing agent; dry distn. gives  $\text{PhCN}$ . The action of 3 mols Br upon  $\text{PhNHN}:\text{CHPh}$  in AcOH-AcONa gives principally II but also some III. C. J. W.

Bromonotocaine. J. FREJKA AND J. VITHA. *Spisy Přírodovědeckou Fakulou Masarykovy University* 1925, No 48, 1-22 — 2,4- $\text{Br(O}_2\text{N)C}_6\text{H}_3\text{Me}$ , m 77-8°, obtained in 90% yield by refluxing  $\text{m O}_2\text{NC}_6\text{H}_4\text{Me}$  with Br and  $\text{FeBr}_3$ , was oxidized by 15 hrs. heating below the h. p with 30%  $\text{HNO}_3$  and a small amt. of Hg and  $\text{KClO}_3$  to 2,4- $\text{Br(O}_2\text{N)C}_6\text{H}_3\text{CO}_2\text{H}$ , m 166-7°, yield 97%. The reduction with  $\text{FeSO}_4$  and  $\text{Ba(OH)}_2$  at 60° or with Fe and HCl at 70° led to 83% 2,4- $\text{Br(H}_2\text{N)C}_6\text{H}_3\text{CO}_2\text{H}$  (I), m 201-2°. Ag salt m 234°, Pb salt m > 300°; Et ester m 125°. Condensed with  $\text{C}_6\text{H}_5(\text{OH})\text{Cl}$ , I yields *p*-amino-*o*-bromobenzoylchloroethanol, m 123-4°, which forms *p*-amino-*o*-bromobenzoyldimethylaminoethanol, m 130-1°, when heated in a sealed tube with 2 mols  $\text{NHMe}_2$ . The following compds were also prepd.: 2,4- $\text{Br(O}_2\text{N)C}_6\text{H}_3\text{COCl}$ , m 132-3°, from the acid and  $\text{PCl}_5$ ; 2,4- $\text{Br(O}_2\text{N)C}_6\text{H}_3\text{CO}_2\text{C}_6\text{H}_5$ , m 59-60°; [2,4- $\text{Br(O}_2\text{N)C}_6\text{H}_3\text{CO}_2$ ] $_2\text{C}_6\text{H}_4$ , m 134-5°, by heating 0.5 hr. the Ag salt and  $\text{C}_6\text{H}_5\text{Br}$  in a sealed tube to 110°; *p*-azo-*o*-bromobenzoic acid, m > 300°, by air oxidation of the hydrazine formed by Zn-NaOH reduction of the  $\text{NO}_2$  compd. It was condensed to the cyclic ester, ethylene *o*-bromo-*p*-azobenzoate by 4 hrs. heating to 110° in a sealed tube with  $\text{C}_6\text{H}_6(\text{OH})\text{Cl}$ . MARY JACOBSEN

The Gattermann aldehyde synthesis in enols. HEINRICH WIELAND AND EUGEN DORRER. *Ber* 58B, 818-20 (1925) — The present work is part of the investigation undertaken in an attempt to bridge the gap which still exists in many reactions between aliphatic and aromatic compds (cf *C. A.* 17, 541). Acetoacetic ester (I) reacts with HCN and HCl gas in the presence of  $\text{AlCl}_3$  just like phenols; although it is present to the extent of more than 90% in the keto form, only the enol form reacts; the product is  $\text{AcCH}(\text{CH NH})\text{CO}_2\text{Et}$  (II).  $\text{C}_6\text{H}_5\text{Ac}$  behaves in the same way, as the  $-\text{CH}:\text{NH}$  group is easily decompd by acids into  $=\text{CHOH} + \text{NH}_3$ , the end product is the same as with phenols. The imines obtained in this new way are not exclusively acidic but also show basic properties, forming well-crystd. HCl salts. They cannot be diazotized and W and D therefore prefer for them the imine rather than the aminomethylene structure.  $\text{AcC}(\text{CHNH}_2)\text{CO}_2\text{Et}$ , suggested by Clausen. The salts with bases, especially the very characteristic Cu salts, are beyond doubt enol salts. As the free imines do not give the  $\text{FeCl}_3$  reaction, they are to be regarded as ketone aldimines. HCl salt of II (20-22 g from 30 g I in 45 cc dry  $\text{C}_6\text{H}_6$ , 30 g  $\text{AlCl}_3$  and 15 cc. anhyd HCN satd at 0° with HCl), m 106° (decompn). Free II, m 50-2° (C gives 55°),  $b_p$  155°.  $\text{AcCHCH NH}$ , from  $\text{Ac}_2\text{CH}_2$ , m 144°. C. A. R.

**Isomerism of *m*-nitrophenylanilinoacetoneitrile.** GUSTAV HELLER AND GERHARD SPIELMEYER. *Ber.* 58B, 838-40(1925).—From 3 g.  $m\text{-O}_2\text{NC}_6\text{H}_4\text{CH}(\text{OH})\text{CN}$  and 1.9 g.  $\text{PhNH}_2$ , allowed to stand 1-2 days in about 10 g. alc. with a little KCN is obtained 2.5 g. of yellow-red rosetts (I) and colorless needles (II), both having the compn.  $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}_4$ . Crystn. from a little alc. or AcOH gives exclusively I in intensely yellow needles,  $m. 102^\circ$ , easily sol. in  $\text{CHCl}_3$ , AcOEt and  $\text{Me}_2\text{CO}$ , difficultly in ligroin; from more dil. alc. solns., which are colorless, II also seps. II is best obtained from PhMe solns. (which are yellow) after adding some ligroin and  $m. 90^\circ$  to a yellow liquid which, after cooling,  $m. 102^\circ$ . Concd. HCl dissolves I quickly and on standing forms a colorless salt; II slowly undergoes the same change without dissolving, this salt becomes greenish about  $180^\circ$  and  $m.$  about  $205\text{--}10^\circ$  to a dark green mass, on standing and in HCl it also gradually becomes green. On treatment with  $\text{Na}_2\text{CO}_3$ , best by pouring the AcOH soln into  $\text{Na}_2\text{CO}_3$ , the salt gives I;  $\text{H}_2\text{O}$  alone also turns it yellow superficially. Heated in AcOH with  $\text{Ac}_2\text{O}$ , both I and II yield an *Ac deriv.*,  $m. 142.5^\circ$ . II is believed to be the normal *m*-nitrophenylanilinoacetoneitrile,  $\text{O}_2\text{NC}_6\text{H}_4\text{CH}(\text{NHPh})\text{CN}$ , and I an isomer  $\text{O}_2\text{NC}_6\text{H}_4\text{CH}(\text{NPh})\text{NCH}$ . *m*-ClC<sub>6</sub>H<sub>4</sub>CH(OH)CN gives only the colorless *m*-chloro-

phenylanilinoacetoneitrile,  $m. 83^\circ$ , indifferent towards concd.  $\text{HCl}$ .

C A R

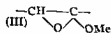
**Higher terpene compounds. XXIV. Ring formation in the sesquiterpene series.** The total synthesis of bisabolene and of a hexahydrocadaline. I. RUXICKA AND E. CAPATO. *Helvetica Chim. Acta* 8, 259-74(1925), cf. *C A* 17, 2419, 19, 648-100 g. of concd. *dl*-nerolidol (I) on shaking 15 hrs. in the cold with 90%  $\text{HCO}_2\text{H}$ , washing and distg., yields approx. 35 g. of farnesene contg. some bisabolene, and 45 g. of a mixt. of unchanged I, farnesol and bisabolol (II), the latter being sepd. and finally converted into the *tri*-HCl salt of bisabolene (III), by treating with  $\text{C}_2\text{H}_5\text{CO}_2\text{O}$ , distg. and passing in dry HCl. III  $m. 79\text{--}80^\circ$  and by heating with  $\text{Ac}_2\text{O}$  and  $\text{NaOAc}$  is converted into bisabolene (IV),  $d_4^{20} 0.8717$ ,  $n_D^{20} 1.4923$ . II  $b_{712} 154\text{--}6$ ,  $d_4^{20} 0.9216$ ,  $n_D^{20} 1.4939$ . If I be boiled with 90%  $\text{HCO}_2\text{H}$  for 1 hr. the double bonds of the aliphatic chain of IV shift so that a 2nd ring closure takes place with the formation of hexahydrocadaline in 30% yields; it  $b_{712} 125\text{--}6^\circ$ ,  $d_4^{20} 0.916$ ,  $n_D^{20} 1.509$ , which properties check those of the natural product. The relation between lab. syntheses and natural synthetic processes are discussed.

Wm. B. PLUMMER

**Irreversible catalysis of unsaturated cyclic hydrocarbons. IV. Contact transformation of  $\alpha$ -pinene, a contribution to the knowledge of dihydropinene.** N. D. ZELINSKII. *Ber.* 58B, 864-9(1925), cf. *C A* 19, 1261.—*l*-Pinene passed in a slow current of  $\text{CO}_2$  at  $190\text{--}200^\circ$  at the rate of 20 drops per min. over palladinized asbestos (previously heated to  $190^\circ$  in H) yielded a mixt. (I),  $b. 166\text{--}75^\circ$ , of cymene, removed by treatment with fuming  $\text{H}_2\text{SO}_4$  (7%), and dihydropinene (II),  $b. 166.5\text{--}7.5^\circ$ ,  $d_4^{20} 0.8467$ ,  $n_D^{20} 1.4589$  (a sample prepd. from pinene by the Sabatier and Senderens method showed  $b_{712} 167\text{--}8^\circ$ ,  $d_4^{20} 0.8457$ ,  $n_D^{20} 1.4559$ ,  $M_D 44.34$ ). The same results were obtained with *d*-pinene. The mixt. (I) obtained in the above expt. was then passed through the same tube in H over Pd at  $200^\circ$  and again at  $150^\circ$ ;  $n_D^{20.5}$  had now fallen to 1.4486 and remained const.; the product b. completely  $169\text{--}70^\circ$  (cor.),  $d_4^{20} 0.8251$ , did not react directly with Br although substitution took place on longer continued action, and was stable towards  $\text{KMnO}_4$ . If the original I was really a mixt. of cymene and II, the cymene on hydrogenation could give only menthane. An equimol. mixt. of II and menthane should show  $n_D^{20} 1.4471$  and analysis of the hydrogenation product (C 86.18, H 14.05%) showed that it was in fact such a mixt. This case of irreversible catalysis, *p*-cymene  $\leftarrow$  pinene  $\rightarrow$  II, furnishes exptl. proof of a change in the structure of a mol. by catalysis. *l*-Pinene passed over palladinized asbestos in H at  $195\text{--}200^\circ$  gives a dihydro product identical with II, but at  $157\text{--}8^\circ$  *d*-pinene yields a dihydro product b.  $169\text{--}9.5^\circ$  (cor.),  $d_4^{20} 0.8351$ ,  $d_4^{20} 0.8341$ ,  $n_D^{20.5} 1.4531$ ,  $[\alpha]_D 2.63^\circ$ ,  $M_D 44.73$ , showing that the catalytic reduction of pinene proceeds differently according to the temp. and the nature of the catalyst.

C A R.

**The constitution and molecular complexity of the hydroxycamphors.** P. KARRER AND NORITAKA TAKASHIMA. *Helvetica Chim. Acta* 8, 242-4(1925).— $\alpha$ -Hydroxycam-



phor (I) yields a Me ether (II) which gives no reaction with  $\text{PhNHNH}_2$  or  $\text{NH}_2\text{NHCO}$ .  $\text{NH}_2$ , showing no CO group to be present. This indicates that the ring of II contains

the grouping III rather than IV. It is probable that I likewise has a structure similar to III. Mol. wt. detns. show I, II,  $\beta$ -hydroxycamphor, and  $p$ -hydroxycamphor to be all dimol. in  $\text{CHBr}_3$ , II being dimol. in  $\text{C}_6\text{H}_6$ , the others monomol. WM. B. PLUMMER

Dynamic isomerism. XVII. Mutarotation of aluminium benzoylcamphor. I. J. FAULENER and T. M. LOWRY. *J. Chem. Soc.* 127, 1080-5 (1925); cf. C. A. 19, 488.—Al benzoylcamphor, plates, m. 227-8°. Soly. in cold  $\text{C}_6\text{H}_6$ , about 5%; in  $\text{CHCl}_3$ , about 30%. In 2.5% soln. in  $\text{CHCl}_3$ ,  $n_D^{20}$  changed from 730° to 772° in 240 min.; in 2.5% soln. in  $\text{C}_6\text{H}_6$ , from 1175° to 1143.8° in 1890 min.; in a satd. soln. in  $\text{Me}_2\text{CO}$ , from 788° (6 min.) to 729° in 24 hrs.; in a satd. soln. in  $\text{C}_6\text{H}_5\text{Br}$ , from 570° (30 min.) to 538° after 9 days. The velocity of mutarotation of this salt falls off much more rapidly than a monomol. law would allow; in  $\text{C}_6\text{H}_6$  it is probably governed by a trimol. law C. J. WEST

Formation of a new dihydroxydiphenyl from resorcinol. BENNOSUKE KUBOTA, YOSHIO FUJIMURA and KASHIWA AKASHI. *Sci. Papers Inst. Phys. Chem. Research (Tokyo)* 2, 185-93 (1925).—Resorcinol vapor passed over the blue oxide of W at 500-50° gave a little  $\text{C}_6\text{H}_6$ ,  $\text{PhOH}$ , diphenylene oxide, and 2% of an acid compd. m. 138.5°. This was identified as a dihydroxydiphenyl by its mol. wt.,  $\text{FeCl}_3$  color reaction, di-Ac deriv. m. 111.5°, and reduction with Zn to diphenylene oxide. Absorption spectra distinguished it from the 4 known dihydroxydiphenyls. Oxidation of its hydrogenated deriv. with  $\text{NaOBr}$  to  $\text{PhCH}(\text{CO}_2\text{H})_2$  proved its structure as 2,6-dihydroxydiphenyl. A. W. FRANCIS

Hydrogenation by formic acid. A. MANJEM. *J. usines gas* 49, 147-50 (1925).— $\text{HCO}_2\text{H}$  (I) if passed together with the vapor of other org. substances over metallic catalysts at 200-400° has a strong reducing action. Aromatic ketones are in all cases smoothly reduced to the corresponding hydrocarbon, aliphatic ketones giving in general the sec. alc., although  $\text{Me}_2\text{CO}$  is an exception, it merely condensing to mesityl oxide and phorone. Diphenylures derivs. may be formed in good yields by passing the vapor of  $\text{RNH}_2$  with I over Ni at 400°; the  $\text{HCONHR}$  which forms below 100° breaks down at 360° to give CO and  $\text{RNH}_2$ , but at 400° combination takes place to form  $\text{CO}(\text{NHR})_2$ , the reaction being quite general. WM. B. PLUMMER

Fluorene series. HEINRICH WIELAND and ERICH KRAUSE. *Ann.* 443, 129-41 (1925); cf. C. A. 17, 754.—The reaction product of  $\text{MeMgBr}$  and fluorenone consists of 9-methylfluoreneol, m. 174° and an isomer, m. 84° (Daufrèsne, C. A. 2, 1273); both show the same chem. reactions.  $\text{HCl}$  in  $\text{Et}_2\text{O}$  gives 9,9-methylchlorofluorene (I), thick, light yellow oil, which, warmed to 80°, yields biphenyleneethylene; it also results by boiling with  $\text{EtOH}$ .  $\text{MeONa}$  gives the 9,9-methylmethoxyfluorene, m. 90°. I and Br in  $\text{AcOH}$  give biphenyleneethylene dibromide (II); this, boiled with  $\text{MeOH-KOH}$  gives 9-oxymethylenefluorene Me ether, m. 106°. Br in  $\text{MeOH}$  gives the compd.  $\text{C}_{16}\text{H}_{11}\text{O}_2\text{Br}$  (a bromodimethoxy compd.), m. 131°. II and  $\text{AcONa}$  in  $\text{AcOH}$  give  $\omega$ -bromobiphenyleneethylene, m. 78°, which adds Br to give  $\alpha,\beta,\beta$ -tribromobiphenyleneethane, m. 127°. II and  $\text{PhNMe}_2$  at 150° give 70% of dibiphenylenebutadiene, orange brown, m. 360°; tetrabromide, m. 150° (decompn.). Biphenyleneethylene in  $\text{Et}_2\text{O}$  adds  $\text{NO}_2$  to give an  $\alpha,\beta$ -dinurobiphenyleneethane, m. 177-8° (decompn.), which with  $\text{NH}_4\text{OH-EtOH}$  gives  $\omega$ -nitrobiphenyleneethylene, orange yellow, m. 132, whose dibromide m. 110°. C. J. WEST

Spectrochemistry and structure of polynuclear aromatic hydrocarbons. K. v. AUWERS and R. KRAUL. *Ann.* 443, 181-91 (1925); cf. A. and Krollpfeiffer, C. A. 17, 1960.—The following values give  $d_n$ ,  $n_n$ ,  $n_D$ , and  $n_D$  at  $t^\circ$ :  $\alpha$ -methylstilbene, 0.9565, 1.58358, 1.59180, 1.61469 at 99.9°; 9-chlorophenanthrene, 1.2167, 1.66300, 1.67393, 1.70285 at 100.5°; 10-Br deriv., 1.4093, 1.67991, 1.69129, 1.72120 at 100.7°;  $\alpha$ -tetrahydrophenanthrene, m. 14°, 1.0707, 1.61880, 1.62660, 1.64684 at 24°. Values are also given for quinoline solns. of stilbene, retene 9-chlorophenanthrene, 9,10-dichlorophenanthrene, dihydrophenanthrene, pyrene and fluoranthene. On the basis of these measurements, the constitution of the several compds. is discussed. C. J. W.

Action of free thiocyanogen upon saturated compounds. E. SÖDERBÄCK. *Ann.* 443, 142-61 (1925).— $(\text{CH}_3\text{SCN})_2$  results in nearly theoretical yield from  $\text{SCN}$  and  $\text{C}_2\text{H}_4$ , in  $\text{C}_2\text{H}_6$ ; anhyd.  $\text{Et}_2\text{O}$  gives poor yields, due to the formation of  $\text{HSCN}$ ; 100 cc.  $\text{C}_2\text{H}_4$  at 17° dissolves 2.08 g.; 100 cc.  $\text{Me}_2\text{CO}$  at 16° dissolves about 13 g.  $\text{PhCH}(\text{SCN})\text{CH}_2\text{SCN}$  results in 17.5 g. yield from 10.4 g.  $\text{PhCH:CH}_2$ ; it crystals with 1 mol.  $\text{C}_6\text{H}_6$ .  $\alpha$ -Stilbene thiocyanide, m. 225-6° (decompn.), results in 7 g. yield from 5 g.  $(\text{PhCH:})_2$ ,  $\text{C}_6\text{H}_6$  and  $\text{SCN}$  in  $\text{C}_6\text{H}_6$  react only in the presence of light (sun or quartz lamp), giving a mixt. of the *trans*-(I) and *cis* acetylenethiocyanates (II); 1 m. 97-8.5; 100 cc.  $\text{Me}_2\text{CO}$  dissolves 13 g. at 16°; 100 cc.  $\text{C}_6\text{H}_6$  at 17° dissolves 2.85 g. II is a liquid,  $d_4^{25}$  1.332, which

solidifies at 0° and then m. 15–7°; miscible in all proportions with EtOH, Et<sub>2</sub>O, Me<sub>2</sub>CO and C<sub>6</sub>H<sub>6</sub>, decomps. above 100°. I may be changed into II by exposing a soln. in C<sub>6</sub>H<sub>6</sub>, satd. with SCN to the light, about 20% being converted in 2 hrs. II in C<sub>6</sub>H<sub>6</sub>, exposed to the light, is transformed into I, about 80% being converted in 2 hrs. Br and I give a di-Br deriv., m. 110–1°, while that from II m. 83.5–4°. The same compds. result from the solid and liquid C<sub>6</sub>H<sub>6</sub>, thus furnishing a basis for the configuration of the products. Phenylacetylene thiocyanate, pale yellow, m. 67–8°; yield practically quant.  $\alpha$ -Tolane thiocyanate, m. 194–5°. The isomeric  $\beta$ -deriv., m. 123–4°, has only been obtained from the dibromide and SCN.

C. J. WEST

Perylene and its derivatives. IX. A. ZENKE, K. FUNKE AND A. PONGRATZ. Ber. 58B, 799–802(1925); cf. C. A. 19, 1568.—To det. the reason for the poor yield (5–9%) of isoviolanthrone (I) from 3,9-dibenzoylperylene (II) baked with AlCl<sub>3</sub>, the dark by-products, which cannot be converted into vat dyes, were studied more thoroughly. As they cannot be crystd., they were purified by pptn. from PhNO<sub>2</sub> with AcOH. They then contained 89.90% C and 6.75% H, indicating that their formation involves quite extensive reduction. The yield of I can be considerably increased (to 30–5%) by impeding this reduction by adding MnO<sub>2</sub> to the AlCl<sub>3</sub>; other oxidizing agents (PbO<sub>2</sub>, HgO, BaO<sub>2</sub>) have a similar though less marked favorable influence. The ring closure can also be easily effected by heating the 4,10-dihalogen derivs. of II with aq. or alc. alkalis at 200–300°, especially if an appropriate solvent is used; with the di-Br compd. short boiling in PhNH<sub>2</sub> with powd. KOH is sufficient, while with the di-Cl compd. a higher temp. (boiling quinoline) is required. This new method can be applied to the synthesis of substitution products of I. Thus, 4,10-dichloroperylene (III), p-ClC<sub>6</sub>H<sub>4</sub>COCl and AlCl<sub>3</sub> allowed to stand 24 hrs. in CS<sub>2</sub> and then refluxed 2 hrs. give 3,9-di-p-chlorobenzoyl-4,10-dichloroperylene, orange-yellow, m. 350°, sol. in concd. H<sub>2</sub>SO<sub>4</sub> with pure blue color and converted by boiling in quinoline with powd. KOH into a dichloroisoviolanthrone, sol. in concd. H<sub>2</sub>SO<sub>4</sub> with pure green color, forms a blue vat with faint brown-red fluorescence, dyes cotton violet-blue and is apparently different from the di-Cl compd. (indanthrene violet 2R extra) obtained by direct chlorination of I. 3,9-Di-p-bromobenzoyl-4,10-dichloroperylene, intensely yellow, m. about 370°, sol. in H<sub>2</sub>SO<sub>4</sub> with steel-blue color, yields in boiling quinoline with powd. KOH a dye almost completely free of halogen which is apparently identical with I.

C. A. R.

Preparation of 2-aminoanthraquinone from phthalic anhydride and chlorobenzene. MAX PHILLIPS. Ind. Eng. Chem. 17, 721–3(1925).—ClC<sub>6</sub>H<sub>4</sub>COCH<sub>2</sub>CO<sub>2</sub>H (I) is obtained in about 77% yield from 0.2 mol. (C<sub>6</sub>H<sub>4</sub>CO)<sub>2</sub>O, 1 mol. PhCl and 0.2 mol. AlCl<sub>3</sub> (molar ratio of (C<sub>6</sub>H<sub>4</sub>CO)<sub>2</sub>O to AlCl<sub>3</sub> 1:1), confirming Heller's conclusion (Z. anorg. Chem. 19, 669(1906)). Decreasing the ratio to 1:0.75 gave a yield of 40%, while with a ratio of 1:2, the yield was 76%. The optimum temp. is 100°. I is practically quant. converted into 2-chloroanthraquinone (II) by heating it at 150° with concd. H<sub>2</sub>SO<sub>4</sub> (ratio 1:6). At 100°, only very small amts. of II were obtained. The optimum conditions for converting II into 2-aminoanthraquinone are: temp. 220° for 6 hrs., concn. of NH<sub>4</sub> with respect to II, 20:1, although 15:1 gave nearly as good results. The NH<sub>4</sub> deriv. obtained under these conditions is 95% pure and the yield is 91%. The addn. of catalysts, such as Cu powder or CuSO<sub>4</sub> to the reaction mixt. is undesirable.

C. J. WEST

1,2-Benzanthraquinone (Sirius yellow G.). E. DE B. BARNETT AND M. A. MATTHEWS. Chem. News 130, 339–40(1925).—1,2-Benzanthracene, pale yellow, m. 158–9° (Elbs, Ber. 19, 2209 gives 141°). 9 (or 10)-Nitro deriv., m. 165°. 1,2-Benzanthraquinone, boiled with Sn in AcOH-HCl, gives a mixt. of 1,2-benz-9-anthrone, m. 170°, whose Bs deriv., m. 171–2°, sepd. by its insoly. in MeEtCO, from 1,2-benz-10-anthrone, which could not be purified but was analyzed as the Bs deriv., m. 202–3°.

C. J. W.

Reaction between aromatic aldehydes and phenanthraquinone in presence of ammonia. A. C. SIRCAR AND N. C. GUHA RAY. J. Chem. Soc. 127, 1048–9(1925).—Heating 1 g. phenanthraquinone (I), 1 g. BzH and 25 cc. concd. NH<sub>4</sub>OH 4 hrs. at 160–70° gives 2-phenylphenanthriminazole, light yellow, m. 295°; o-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CHO gives the 2'-nitro deriv., light yellow. o-HOC<sub>6</sub>H<sub>4</sub>CHO and I in AmOH at 10–15°, treated with dry NH<sub>3</sub> for 15 min., give 2'-hydroxy-2-phenylphenanthroxazole, m. 231–3°; it develops a bluish green fluorescence with concd. H<sub>2</sub>SO<sub>4</sub>. m-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CHO gives the 3'-nitro deriv., light yellow, m. 248°, and gives a greenish yellow color in concd. H<sub>2</sub>SO<sub>4</sub>. 2'-Nitro deriv., yellow, m. 166°, sol. in concd. H<sub>2</sub>SO<sub>4</sub> with a yellowish brown color.

C. J. WEST

Additive formation of four-membered rings. VII. Synthesis and division of some dimethylene-1,3-oxamines. C. K. INGLIS. J. Chem. Soc. 127, 1141–5(1925); cf. C. A. 19, 1421.—Rings of this type are produced from CO compds. and azomethines and

their division in the 2 possible directions may give rise to double-bonded products of the same 2 classes  $\text{XYC-NZ} + \text{PQC-O} \rightleftharpoons \text{XYC-NZ-CPQ-O} \rightleftharpoons \text{XYC:O} +$

$\text{PQC-NZ}$  This reaction can be detd. completely in either direction in favor of an insol participant, in a solvent, however, in which all the participants in the balanced reaction are readily sol an equil is attained which can be approached from either end As representative of the latter class there are discussed the reaction between  $p\text{-O}_2\text{NC}_6\text{H}_4\text{CHO}$  and  $m\text{-O}_2\text{NC}_6\text{H}_4\text{CH NCH}_2\text{C}_6\text{H}_4\text{NO}_2$ ,  $p\text{-O}_2\text{NC}_6\text{H}_4\text{CHO}$  and  $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH NCH}_2\text{C}_6\text{H}_4\text{NO}_2$ ,  $p\text{-O}_2\text{NC}_6\text{H}_4\text{CHO}$  and  $m\text{-O}_2\text{NC}_6\text{H}_4\text{CH NCH}_2\text{C}_6\text{H}_4\text{NO}_2$ ,  $p\text{-O}_2\text{NC}_6\text{H}_4\text{CHO}$  and  $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH NCH}_2\text{C}_6\text{H}_4\text{NO}_2$ ,  $m\text{-O}_2\text{NC}_6\text{H}_4\text{CHO}$  and  $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH NCH}_2\text{C}_6\text{H}_4\text{NO}_2$ . The first class includes the following reactions  $p\text{-O}_2\text{NC}_6\text{H}_4\text{CHO} + \text{PhCH NCH}_2\text{C}_6\text{H}_4\text{NO}_2$  (I),  $m\text{-O}_2\text{NC}_6\text{H}_4\text{CHO} + \text{I}$ ,  $p\text{-O}_2\text{NC}_6\text{H}_4\text{CHO} + \text{PhCH NCH}_2\text{C}_6\text{H}_4\text{NO}_2$  (II),  $m\text{-O}_2\text{NC}_6\text{H}_4\text{CHO} + \text{II}$ . In no case was the cycloid isolated

C. J. WEST

Preparation of fufural from Japanese rice bran. HARUKAZU UTAKE. *Report Osaka Ind. Research Lab (Japan)* 5, No. 16, 1-11(1925).—The effect of HCl and  $\text{H}_2\text{SO}_4$  as catalyzers in La Forge and Mains' method (C. A. 17, 3823), of prep. fufural was investigated with Japanese rice bran. The sample used contained 11.99%  $\text{H}_2\text{O}$ . The % compn. of the solids was pentosan 17.92% (10.52% as fufural), fat 0.44%, ash 14.09% (silica 6.31%), crude protein 3.69%, crude fiber 43.64% (ash in the fiber 2.75%), and other N substances 20.22%. The conclusions are HCl is a better catalyst than  $\text{H}_2\text{SO}_4$  with the rice bran, but  $\text{H}_2\text{SO}_4$  may be better for industrial use; with the latter, 9-10% fufural can be obtained from the air-dried sample of bran. With 100 lbs steam pressure, per sq in., 1 hr treatment is the best; the amt of the acid should be about 0.4% of the total sample, in such a diln as to make about 10 times the vol of the bran. By this method, U obtained besides fufural, 0.03% AcH, 0.07% volatile org acids, 2% sugar and a trace of MeOH

S. T.

Action of formaldehyde and of substituted alcohols upon pyrrole derivatives and a new synthesis of kryptopyrrolecarboxylic acid. H. FISCHER AND C. NENITZESCU. *Ann* 433, 113-29(1925).—2,4-Dimethyl-3-carbethoxy-5-hydroxymethylpyrrole, m. 119°, results by warming to 80° for 1 hr 6 g 2,4-dimethyl-3-carbethoxypyrrole (I) and 18 cc. 40% HCHO contg a couple of drops of NaOH, heated to 130°, it evolves HCHO, boiled with AcOH HCl, it gives a dirty red color. 2,5-Dimethyl-3-carbethoxypyrrole (II) (1.7 g) in EtOH, 3 cc 40% HCHO and 1.2 g KCN in  $\text{H}_2\text{O}$  give the corresponding 4-hydroxymethyl deriv, m. 131-2°, HCl AcOH gives a deep violet color; in concd soln. absorption was observed in all colors but the red, in dil soln., a max. was observed at 575 $\mu$ . When 3 g II, 9 cc HCHO and a few drops 30% NaOH are heated, there results tris-[1-hydroxymethyl-2,5-dimethyl-3-carbethoxypyrrole], m. 169° (decompn); on heating the Ehrlich reaction is strongly positive. Heated to 180° or treated with concd  $\text{NH}_4\text{OH}$  in boiling alc, it gives bis-[2,5-dimethyl-3-carbethoxypyrrole-4] methane, m. 230°. Tris-[1-hydroxymethyl-2,4-dimethyl-3-carbethoxypyrrole] m. 175° (gas evolution). Acetylpyrrole and excess HCHO give the corresponding 3-Ac deriv, m. 185°. 2,4-Dimethyl-5-carbethoxypyrrole (III) and excess HCHO give directly bis-[2,4-dimethyl-5-carbethoxypyrrole-3] methane, m. 229-30°. 2,5-Dimethyl-3-carbethoxy-4-acetaminomethylpyrrole, m. 158°, results from II and a soln. of methylolacetamide (*Ann*, 343, 265). The 4-chloroacetaminomethyl deriv, m. 152°, possesses no basic properties. No definite compds could be isolated from the products of hydrolysis. 2,4-Dimethyl-3-carbethoxy-5-chloroacetaminomethylpyrrole, m. 191° (decompn). Condensation of trimethylpyrrole with methylolchloroacetamide gave bis-[2,3,5-trimethylpyrrole-4]-methane (IV), m. 197°. 2,5-Dimethyl-3-carbethoxy-4-diethylaminomethylpyrrole was analyzed as the perchlorate, which explodes on heating. The corresponding 4-N-piperidinomethyl deriv. explodes on heating. IV is also formed by heating trimethylpyrrole with HCHO and  $\text{C}_2\text{H}_5\text{N}$ . III and MeOCH(CO $_2$ Et), in EtOH-HCl give di-Et-[2,4-dimethyl-5-carbethoxypyrrole-3]  $\beta$ -methylmalonate, m. 107°, saponified by NaOH to the free acid, m. 185°; heating above the m p gives 2,4-dimethyl-5-carbethoxypyrrole-3-propionic acid, m. 152°. Boiling with 4 mols NaOH in a little  $\text{H}_2\text{O}$  gives kryptopyrrolecarboxylic acid in 70% yields, picrate, m. 156°, its absorption spectrum is given. The isonitroso deriv. m. 215°. Trimethylpyrrole and HCN, satd with HCl, give 2,4,5-trimethylpyrrole-3-aldimine-HCl, yellow, which with cold  $\text{NH}_3$  gives 2,4,5-trimethyl-3-formylpyrrole. Dimethylpyrrole under the same conditions gives 2,4-dimethylpyrrole-aldehyde and a compd.  $\text{C}_8\text{H}_{11}\text{N}_3$ , m. 174°, strongly electr. needles.

C. J. WEST

"Indin," isoindigo, "hydindin" and the inner anhydride of  $\alpha,\beta$ -bis-[ $\sigma$ -aminophenyl]malic acid. LUOWIG SANDER. *Ber* 58B, 820-4(1925); cf. Friedländer and S. C. A. 18, 2701, Laurent, *J prakt Chem* [II], 25, 430(1842).—L's "indin" is really isoindigo (I) and his "hydindin" is  $\alpha,\beta$  bis [ $\sigma$ -aminophenyl]malic bislactam. In

attempting to recryst. his "sulfesatyde" (III) it was found that it is converted into I not only by the action of dil. alc. NaOH but also by long standing in cold  $C_6H_5N$  or short warming with it. By analogy with the reduction of isatin anilide to indigo blue through  $\alpha$ -thioisatin (IV), in the reduction of isatin to I with  $Na_2S$  or  $H_2S$   $\beta$ -thioisatin (V) might be assumed to be an intermediate product. While, however, the conversion of IV into indigo blue is accompanied by the liberation of elementary S, in that of III into I  $H_2S$  almost exclusively is set free. III is therefore not V but a reduction product of it, a view confirmed by the fact that in its formation from isatin and  $H_2S$  much elementary S is set free. It is exceedingly probable that III is 3-mercaptioxindole or 3-thiodioxindole,  $C_8H_7C(SH).C(OH)NH$ . C. A. R.

**Indigoid dyes.** LUDWIG SANDER *Ber* 58B, 824-34 (1925).—2-[Thionaphthene]- and 2-[indole]-1'-[3-hydroxynaphthalene]indolignone (I,  $R = S$  and  $NH$ , resp.), yield with  $\alpha$ - $C_6H_4(NH_2)_2$  the 1st and simplest representatives of a new class of dyes (III), which may be considered as azines as well as indigoids. They form with mineral acids quite stable salts which are more deeply colored than the dye bases. Their orange-yellow, i. e., very light, color is striking, for their components are violet and other indigoid dyes derived from I by replacement of the HO group by a basic residue (e. g., IV) are blue to blue-green. Dyes of the type IV are obtained from naphthoquinone anils and hydroxythionaphthene (V). Such anils can readily be prepd from  $\alpha$ -naphthols and  $PhNO$  if  $NH_2$  be used as the condensing agent instead of  $NaOH$  as directed by Euler (*Ber.* 39, 1035 (1906)); even ammonaphthols can be converted into the quinone anils in this way if the  $NH_2$  group is protected by acetylation. With V these anils may react in 2 ways: (1) the anil group is replaced by the V residue with elimination of  $PhNH_2$ , or (2) the V residue replaces the atom or group on the  $\sigma$ -C atom to the C O group while the anil residue is reduced to  $PhNH$  with formation of a dye of type VI (C. A. 18, 2704). When the atom on this  $\sigma$ -C atom is H, the reaction proceeds according to (2), and the acetylamionaphthoquinone anils react in the same way. The dye obtained from 5-acetylamino-1,4-naphthoquinone 4-anil (VII) is considerably more basic than that (VIII) obtained from the 6-AcNH isomer and analysis leaves no doubt that a pyrimidine ring has been formed and that the dye is a perimidine (IX). Likewise, in the reduction product of VII the tendency to pyrimidine ring formation is so great that the primary product cannot be isolated while the perimidine (X) can easily be obtained pure. Unlike  $\alpha$ -naphthol,  $\alpha$ -anthrol cannot be smoothly condensed with  $PhNO$ , while acenaphthenone and anthrone can be condensed almost quantitatively and the resulting anils readily yield with V dyes of the types XI and XII. III ( $R = S$ ), decmps. 250-60°; *HCl* salt, chocolate-brown, dissociates easily, dissolving in hot  $AcOH$  with orange-yellow color and regeneration of III, which is insol. in cold aq. alkalis but dissolves in cold alc. NaOH with violet color; concd.  $H_2SO_4$  carbonizes it even in the cold. III ( $R = NH$ ), m. about 290° (blackening), decmpd. by long heating in  $PhNO$ ; *HCl* changes the orange-yellow soln. in  $AcOH$  to red but on neutralization III seps unchanged; it dissolves in cold concd.  $H_2SO_4$  with red color and on diln. remains dissolved as the sulfate but is reprecip. by addn. of  $NH_4OH$ . 1,4-Naphthoquinone 4-monoanil (XIII) is obtained in 8.6 g. yield from 5.8 g.  $\alpha$ -naphthol in cold concd. alc. soln. and 2 cc. concd.  $NH_4OH$  treated in the course of 30 min. with 4.3 g.  $PhNO$  in 50 cc. of 96% alc. VII, brown-yellow, m. 210° (decompn.); 6-AcNH isomer, brown-red, m. 210-20° (decompn.), slowly decmps. in the air. 6-Acetylamino-1-naphthol, from 16 g. com. 1,6- $C_{10}H_6(OH)NH_2$  in a little  $AcOH$  and 7 g.  $Ac_2O$  boiled a few min., m. 100°. Anthraquinone monoanil (5.2 g. from 4 g. anthrone in 100 cc. abs. alc. at 60°, 2 cc. concd.  $NH_4OH$  and 2 cc. 2 N  $NaOH$  quickly treated with 2.1 g.  $PhNO$  in 20 cc. abs. alc. at 30°), yellow-red, m. 123°, decmpd. by short warming with 50%  $H_2SO_4$  into  $C_6H_4(CO)_2C_6H_3$  and  $PhNH_2$ . Acenaphthenequinone monoanil (yield, 86%), yellow, m. 189-90°. 1-Phenyl-2-methyl-7-hydroxyperimidine (X), from VII with  $SnCl_4$  in cold alc. and fuming  $HCl$ , m. above 300°, is very little sol. in  $H_2O$  and oxidizes with extreme ease, turning brown, in alk. media; *HCl* salt. The condensation of the anils with V is best effected in concd. alc. soln. with a little  $AcOH$  as the condensing agent; it is advisable to use only slightly more than 0.5 mol. V per mol. anil. 0.5 of the anil being used up to remove the 2 atoms of H set free in the condensation. 8-[1-Phenyl-2-methylperimidine]-2'-[thionaphthene]indigo (IX), dark violet with metallic luster, sel. in neutral org. solvents with faint bluish green, in  $AcOH$  and  $Ac_2O$  with violet-blue to pure blue color (depending on the concn.);  $AcOH$  changes the green  $PhNO$  soln. to blue, which on addn. of a neutral solvent (like xylene) gradually changes back to green; the IX dissolves in cold concd.  $H_2SO_4$  with pure green color completely decolorized by addn. of  $H_2O$  with pptn. of a blue-violet flocculent sulfate, which, on neutralizing the liquid with  $NH_4OH$ , becomes bluish green but on addn. of concd.  $HCl$



$\text{Ac}_2\text{O}$ , dissolved in 3% alkali and treated with  $\text{K}_3\text{Fe}(\text{CN})_6$ , it gives 5,5'-dibromo-6,6'-dimethoxy-2,2'-bisoxylthionaphthene (III), dark red, m. 355-60°; the dye is reprecipitated from its deep blue soln. in concd.  $\text{H}_2\text{SO}_4$  in a gelatinous state very suitable for the prepn. of the vat, which is pale yellow and dyes cloth a good scarlet. The  $\text{PhNO}_2$  soln. shows an absorption band with a max. at  $\lambda = 529$ ; "Helindone Fast Scarlet R" shows a similar band with a max. at  $\lambda = 520$ . II and isatin give the compd.  $\text{C}_{17}\text{H}_{10}\text{O}_2\text{NBrS}$  (IV), which has a much bluer shade than III; its  $\text{H}_2\text{SO}_4$  soln. is purple but its dyeing properties are unsatisfactory, probably on account of further reaction during reduction. II and acenaphthenequinone give an orange powder (V), m. 337°, giving dark brown solns. in concd.  $\text{H}_2\text{SO}_4$  and dyeing cloth a good orange from a bright blue bath.

C. J. WEST

**Indazoles from o-nitromandelonitrile.** GUSTAV HELLER AND GERHARD SPIELMEYER. *Ber.* 58B, 834-8 (1925).— $\text{o-O}_2\text{NC}_6\text{H}_4\text{CH}(\text{OH})\text{CN}$  (5 g.) in an equal wt. of alc. allowed to stand 2-3 days with 3 g.  $\text{PhNH}_2$  and about 0.01 g.  $\text{NaOAc}$  gives 3-3.5 g. 2-phenyl-3-cyanoindazole N-oxide,  $\text{O}_2\text{N.C}_6\text{H}_4\text{:C}(\text{CN}).\text{NPh}$  (I) (also obtained from 1.51

g.  $\text{o-O}_2\text{NC}_6\text{H}_4\text{CHO}$ , 1.3 g.  $\text{PhNH}_2\text{HCl}$ , a particle of  $\text{NaOAc}$  and 0.7 g.  $\text{KCN}$  in about 20 cc. alc.), light yellow, m. 190°, seps. from  $\text{C}_6\text{H}_6$ ,  $\text{CHCl}_3$  and  $\text{AcOH}$  in colorless solvated crystals which, when pressed out, become yellowish and opaque in the air; it is stable towards acids and not easily hydrolyzed, 3 g. in  $\text{AcOH}$  with  $\text{Zn}$  dust gives 2 g. 2-phenyl-3-cyanoindazole (II), m. 105°, hydrolyzed by 75%  $\text{H}_2\text{SO}_4$  on the  $\text{H}_2\text{O}$  bath to the 3- $\text{CO}_2\text{H}$  acid (III), m. 200° (loss of  $\text{CO}_2$  and formation of 2-phenylindazole (IV)), and the amide, m. 247-8°; the latter is formed almost exclusively with 95%  $\text{H}_2\text{SO}_4$  at 160° and is only slowly hydrolyzed by boiling alkalis. 2-p-Tolyl isomer of I, obtained with  $p\text{-MeC}_6\text{H}_4\text{NH}_2$ , m. 198-9°; of II, m. 135°; of III, m. 195° (loss of  $\text{CO}_2$ ). 2-p-Chlorophenyl analog of I, m. 201°; of II, m. 159°; of III, m. 198° (loss of  $\text{CO}_2$ ). 5-Cl deriv. of I, yellow, m. 226-8°; of II, m. 147-8°; of III, m. 200° (loss of  $\text{CO}_2$ ); of IV, m. 147°, sol. in concd.  $\text{HCl}$  only on heating. Mol. amts. of  $\text{o-O}_2\text{NC}_6\text{H}_4\text{CH}(\text{OH})\text{CN}$  and  $\text{PhNHNH}_2$  allowed to stand in alc. yield  $\text{o-O}_2\text{NC}_6\text{H}_4\text{CH:NNHPh}$ ; the nitrile, satd. in  $\text{Et}_2\text{O}$  with dry  $\text{HCl}$ , yields 3,6-bis-[o-nitrophenyl]-2-oxo-1,2-diazine 1,2-dihydrate,  $\text{O}_2\text{NC}_6\text{H}_4\text{:C:CH:N:C}(\text{C}_6\text{H}_4\text{NO}_2).\text{CO.NH}$ ,

yellow, m. 193°, sol. in fuming  $\text{HCl}$  (from which it is reprecipitated by  $\text{H}_2\text{O}$ ) and in hot dil.  $\text{NaOH}$  and  $\text{Na}_2\text{CO}_3$ , being reprecipitated by acids; it is unchanged by 75%  $\text{H}_2\text{SO}_4$  at 100° or concd.  $\text{HCl}$  at 160-70°.

C. A. R.

**Benzothiazole series. III.** The pseudo-bases of the 1-substituted benzothiazole quaternary salts. L. M. CLARE. *J. Chem. Soc.* 127, 973-5 (1925); cf. C. A. 18, 83.—Oxidation of 1-methylbenzothiazole-Mel in 10%  $\text{NH}_3$  for 6 weeks gave 2,2'-diacetyl-methylaminodiphenyl disulfide, m. 171°, also obtained from  $\text{Ac}_2\text{O}$  and the corresponding disulfide. The ethiodide (I) gave the corresponding Et deriv., m. 103°. 2,2'-Diethyl-ethylamino-5,5'-dimethyldiphenyl disulfide, m. 129°. In the titration of I with  $\text{NaOH}$ , the red color of the phenolphthalein persists for some secs. after each fresh addn. of alkali; this time interval becomes so prolonged when nearly the 2 equivs. of alkali required by theory have been added that a sharp end point cannot be obtained. 1-Phenylbenzothiazole-Mel, yellow, m. 218°. Oxidation of its  $\phi$ -base with I gives 2,2'-dibenzoyl-methylaminodiphenyl disulfide, m. 164°. Boiling 90%  $\text{HCO}_2\text{H}$  and bis-2-methylbenzothiazoline-1,1-spiran give 2-methylbenzothiazolone, thus confirming its formula. The filtrate contains benzothiazole methoformate, since oxidation gives 2,2'-diformyl-methylaminodiphenyl disulfide, m. 106-7.5°.

C. J. WEST

**Formation of quinonimides and phenoxazones from o-aminophenols.** K. v. AUWERS, E. MURBE, K. SÄDERWEIN, G. DENTES AND J. SCHORNSTEIN. *Fortschritte der Chemie, Physik und physik. Chem.* 18, No. 2, 37-77 (1924).—3,5- $\text{Me}_2\text{C}_6\text{H}_3\text{OH}$  (I) in  $\text{AcOH}$  and  $\text{Cl}$  give 66% of the p-Cl deriv. (II), m. 114-5°, a concd. soln. in  $\text{CCl}_4$  gives a mixt. of mono- and di-Cl derivs. (32.2% Cl), m. 77.5-85°, whose *Bz* deriv., m. 113-4°. Completely satg. I in  $\text{AcOH}$  with  $\text{Cl}$  gives 1,3-dimethyl-2,4,4,6-tetrachloro-2,6-cyclohexadien-5-one (or 1,3-dimethyl-2,2,4,6-tetrachloro-3,6-cyclohexadien-5-one), m. 106-7°, decompd. by warm  $\text{NaOH}$ . II and  $\text{Me}_2\text{SO}$  give the *Me* ether, *b.p.* 117°, m. 22.5-35°, which, with  $\text{AcCl}$  and  $\text{AlCl}_3$  in  $\text{CS}_2$ , gives the o-Ac deriv., m. 76-7° (oxime, m. 134-5°). Heated with  $\text{AlCl}_3$  at 140-50°, there results p-chloro-o-aceto-sym-m-xyleneol, m. 109° (oxime, m. 138.5°). The oxime, boiled with 1:1  $\text{HCl}$ , yields o-amino-p-chloro-sym-m-xyleneol (III), m. 148-9°, quickly turns yellow in the air. The o- $\text{NO}_2$  deriv. of II, egg-yellow, m. 87-9°, also gives III on reduction. Oxidation of III in  $\text{NaOH}$  by  $\text{O}$  or by air in  $\text{H}_2\text{O}$  soln. gives 3,5-dimethyl-2-amino-1,4-benzoquinone 4-[2,4-dimethyl-3-chloro-6-hydroxyphenyl]imide, brownish yellow prisms or ochre-yellow powder, m. 188-9°, sol. in  $\text{EtOH}$ - $\text{NaOH}$  with a yellow red color and is pptd. unchanged by  $\text{H}_2\text{O}$ ; diln. of

the brownish  $\text{H}_2\text{SO}_4$  soln gives a pale green fluorescence. 2,6,4- $\text{Me}_3(\text{HO})\text{C}_6\text{H}_2\text{CH}\cdot\text{NOH}$  with  $\text{AcOH}$   $\text{AcONa}$ , followed by sapon, gives *p*-cyano-*sym-m* xyleneol, m. 174-5°, whose *o*- $\text{NO}_2$  deriv, pale yellow, m. 136.5-7.5°; reduction gives the *o*- $\text{NH}_2$  deriv, m. 165-6°, which is unchanged by oxidizing agents. Hemimelliteneol Me ether, b. 220.5°,  $\text{AcCl}$  and  $\text{AlCl}_3$  give *o*-acetohemimelliteneol, m. 83.5-4.5°; the oxime, m. 147°, with  $\text{HCl}$  gives *o*-aminohemimelliteneol (IV), m. 164-5°, and traces of 2,4,5,6-tetramethylbenzoxazole, m. 70-1°. *o*-Nitrohemimelliteneol, yellow m. 96-8°. Oxidation of IV did not give definite products. *o*-Aminoisopropylbenzene, m. 157-8°, on oxidation with air gives 3,5,6-trimethyl-2-amino-1,4-benzoquinone 4-[2,4,5-trimethyl-6-hydroxyphenyl]imide, deep yellow, m. 177-8°,  $\text{HCl}$  salt, red;  $\text{H}_2\text{SO}_4$  gives a Bordeaux-red color.  $\text{m-ClC}_6\text{H}_4\text{NH}_2$  gives a mixt of 5,2- $\text{Cl}(\text{O}_2\text{N})\text{C}_6\text{H}_3\text{OH}$  (V) and 5-chloro-4-nitrophenol, pale yellow, m. 120-1° (av. yields, 30-35 and 25-30%). Reduction of V with  $\text{SnCl}_2$  and  $\text{HCl}$  gives 5-chloro-2-aminophenol, m. 153-4° ( $\text{HCl}$  salt, m. 226-7° (decompn.); di-*Bs* deriv, m. 140°). Oxidation with air gives 7-chloro-3-aminophenoxazone (VI), dark reddish violet, m. 288°, *Ac* deriv, orange-yellow, m. 325°. With 2- $\text{HOCH}_2\text{CHO}$  there results 3-[2-hydroxybenzylidene]amino-7-chlorophenoxazone, nearly black, with metallic luster, m. 310-1°. VI and 5,2- $\text{Cl}(\text{H}_2\text{N})\text{C}_6\text{H}_3\text{OH}$   $\text{HCl}$  give 2,6-dichlorotriphenyldioxazine, wine red, sublimes above 360°, and gives a deep blue concd  $\text{H}_2\text{SO}_4$  soln. 5-Bromo-2-nitrophenol, m. 41.5-2.5° (35-40% yields), the 4-nitro deriv, yellow, m. 129-30°. 5-Bromo-2-aminophenol, pale rose, m. 146-7°. 7-Bromo-3-aminophenoxazone, dark red, m. 285-6°; 2,6-dibromotriphenyldioxazine, brown flakes, sublimes above 360°; concd.  $\text{H}_2\text{SO}_4$  soln, deep blue. 2-Aceto-3,5-dichlorophenol (VII), m. 49-50° (35-40%); the 4 *Ac* deriv, m. 117-9° (yield, 30%). Oxime of VII, m. 140-1°;  $\text{HCl}$  gives 3,5-dichloro-2-aminophenol, m. 132-3° (60% yield) and some 2-methyl-4,6-dichlorobenzoxazole, m. 50-1°. 3-Amino-4,5,7-trichlorophenoxazone, brick red, m. 286-7°. 4-Aceto-3,5-dibromophenol, m. 141-2°. 2-*Ac* deriv, m. 96-7°, oxime, m. 139-40°. 3,5-Dibromo-2-aminophenol, m. 142-3°; the anhydro-base, 2-methyl-4,6-dibromobenzoxazole, m. 100-2°. 3-Amino-4,5,7-tribromophenoxazone, wine-red, m. 305-6°. 3-Hydroxy-4-nitrobenzaldoxime, light yellow, m. 161°. 5-Cyano-2-nitrophenol, brownish yellow, m. 121°; *Ac* deriv, m. 107°. 5-Cyano-2-aminophenol, light yellow, m. 149-50°, di-*Bs* deriv, m. 165-6°. Oxidation did not give characteristic compds. 5-Nitro-2-aminophenol benzoate, m. 266-7°; oxidation of the free phenol gave indefinite products. 2-Methyl-5-chlorophenol, m. 73-4°. 6-Nitro deriv, Au yellow, m. 54.5-5° (the *p*-deriv., m. 144-5°); 6-amino deriv, m. 151°; oxidation gave 1,8-dimethyl-4,5-dichloro-3-aminophenoxazone, blood-red, m. 309-9°. 2-Methyl-3-chloro-6-aminophenol, m. 102°, oxidation gave 1,8-dimethyl-7-chloro-3-aminophenoxazone, dark red, m. 278-9°, *Ac* deriv, orange red, m. 304-5°. The structure of *o*-nitro-*p*-xyleneol, whose *Bs* deriv, m. 79-80°, follows from its reduction by  $\text{SnCl}_2$  to 2-phenyl-4,7-dimethylbenzoxazole, m. 75°. *o*-Amino-*p*-xyleneol, m. 149-50°, *N*-*Bs* deriv, m. 210-1°; dibenzoate, m. 178-9°. 1,4,5,8-Tetramethyl-3-aminophenoxazone, dark bronze-red, m. 275-6°; *Ac* deriv, bright red, m. 223-9°. *p*-Bromo-*o*-nitro-*p*-xyleneol, m. 102-3°; the *o*-amino deriv, m. 135.5-6° (di-*Bs* deriv, m. 217-8°); oxidation expts gave indefinite results. *o,o*-Diamino-*sym-m*-xyleneol, m. 179-80°; oxidation gave no definite results. 2,1- $\text{H}_2\text{N}\cdot\text{C}_6\text{H}_4\text{OH}$  gave no definite product on oxidation; the crude product gave a "semicarbazone,"  $\text{C}_6\text{H}_7\text{O}_2\text{N}_3$ , of indefinite m. p. Thus, in general,  $\text{o-NH}_2\text{C}_6\text{H}_4\text{OH}$  contg. in the *m*-position to the  $\text{HO}$  group a strongly negative group do not give oxidation products.

C. J. WEST

A general method of formation of 4-alkyl-1-phenyl-1,2,3-triazoles. ALFRED BERTHO *Ber.* 58B, 859-64 (1925).—When  $\text{PhN}_3$  is boiled with alc.  $\text{NaOEt}$ ,  $\text{N}$  is slowly evolved, with 3 mols  $\text{NaOEt}$  to 1 of  $\text{PhN}_3$  at 91° the evolution of the  $\text{N}$  ceases in 115 hrs and the reaction product consists chiefly of  $\text{PhNH}_2$  and 1-phenyl-1,2,3-triazole (I), together with a small amt of an acid substance (II), sepg from  $\text{PhNO}_2$  in reddish white prisms, m. 272°, and some  $\text{PhOH}$  and  $\text{NH}_3$ . The yields of  $\text{PhNH}_2$ , I and  $\text{N}$  indicate that the reaction proceeds almost quant. according to the scheme  $2\text{PhN}_3 + \text{EtONa} = \text{PhN}_2\text{H} + \text{I} + \text{N}_2 + \text{NaOH}$ , 0.5 of the  $\text{PhN}_3$  yields the  $\text{N}_2$  and the resulting radical  $\text{PhN}=\cdot$  is reduced to  $\text{PhN}_2\text{H}$ , the necessary  $\text{H}_2$  probably being obtained from that C atom of the  $\text{EtONa}$  which also carries the  $\text{ONa}$ ; the intermediate anti-body (cf. C. A. 18, 3363) thus formed, which may be assumed to have the isomeric form  $\text{CH}_2\cdot\text{CHONa}$ , splits off  $\text{NaOH}$  and under the influence of the excess of  $\text{NaOEt}$  condenses with the other 0.5 of the  $\text{PhN}_3$  to form I. By using the alcoholates of other primary aliphatic alcs, 4-alkyl derivs of I may be obtained in good yields. The higher the b. p. of the alc., the sooner is the reaction complete; cessation of the evolution of  $\text{N}$  shows when the reaction is ended. In non boiling solns, in which the reaction proceeds more slowly, the yield of triazole is small. With alcoholates of secondary alcs, the azide residue is not hydrogenated to a condensable intermediate anti body and is finally converted

entirely into  $\text{PhNH}_2$  without any marked resinification. Primary alcs. without any alcoholate also do not react; together with the formation of  $\text{PhNH}_2$ , there is much resinification, however. The 4-alkyl derivs. of I are very weak, low-melting bases of moldy odor, faintly yellowish in the fused state and easily become decolorized on standing; they are somewhat volatile with  $\text{H}_2\text{O}$  vapor and form unstable salts with mineral acids. II is obtained not only with  $\text{NaOEt}$  but with all other alcoholates. I (17.7 g. from 50 g.  $\text{PhN}_3$ ), m.  $56^\circ$ ,  $b_{10}$ ,  $172-4^\circ$ , mol. wt. in freezing  $\text{C}_6\text{H}_6$ , 146.6. 4-Alkyl derivs. of I: Me (1.6 g. from 3.5 g.  $\text{PhN}_3$  and  $\text{PrONa}$  after 24 hrs. boiling), m.  $81^\circ$ , greatly depresses the m. p. of the 5-Me deriv., m.  $64^\circ$ . Et (1.4 g. from 6.9 g.  $\text{PhN}_3$  and  $\text{BuONa}$  after 5.5 hrs.), m.  $19^\circ$ ,  $b_{12}$   $169-70^\circ$ . iso-Pr (2 g. from 8.8 g.  $\text{PhN}_3$  and iso-AmONa after 3-4 hrs.), m.  $29^\circ$ ,  $b_{12}$   $183-5^\circ$ . C. A. R.

Aryl azides. V. ECG. BAMBERGER. *Ann.* 443, 192-210 (1925), cf. C. A. 19, 1252.—Further exptl. details of work theoretically discussed in C. A. 15, 3987. The following systems are reported:  $\text{H}_2\text{SO}_4$  with  $p\text{-MeC}_6\text{H}_4\text{N}_3$ , with  $\text{PhN}_3$ , with  $\text{PhN}_3 + \text{PhOH}$ ,  $\text{EtOH}$ - or  $\text{MeOH-H}_2\text{SO}_4$  with  $\text{PhN}_3$ , with  $o\text{-MeC}_6\text{H}_4\text{N}_3$ , with  $m\text{-MeC}_6\text{H}_4\text{N}_3$ , with  $p\text{-xylyl azide}$ ;  $\text{HCl}$  with  $\text{PhN}_3$ , with  $o\text{-MeC}_6\text{H}_4\text{N}_3$ , with  $p\text{-xylyl azide}$ ,  $\text{HBr}$  with  $p\text{-xylyl azide}$ . The action of  $\text{HCl}$  and of  $\text{H}_2\text{SO}_4$  upon  $p\text{-ClC}_6\text{H}_4\text{N}_3$  and the action of  $\text{H}_2\text{SO}_4$  and  $p\text{-BrC}_6\text{H}_4\text{N}_3$  were studied. *Chloroxylylidine* ( $2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{NH}_2$ ) m.  $40-1^\circ$ ; *Ac deriv.* m.  $205.5-6.5^\circ$ ; *phenylurea* m.  $243^\circ$ . The synthesis from  $2,4\text{-Me}_2\text{C}_6\text{H}_3\text{NH}_2$  is described. C. J. WEST

Synthesis of pyrylium salts of anthocyanidin type. VI. Polyhydroxyflavylium salts related to chrysin, apigenin, luteoflavin, luteolin, galangin, fisetin and morin. D. D. PRATT AND ROBERT ROBINSON. *J. Chem. Soc.* 127, 1123-38 (1925); cf. C. A. 19, 1141.—*Phenyl 2-hydroxy-4,6-dimethoxystyryl ketone*, pale yellow, m.  $136^\circ$ , in 5 g. yield from 6 g.  $2,4,6\text{-HO}(\text{MeO})_3\text{C}_6\text{H}_2\text{CHO}$  and 4 g.  $\text{BzMe}$  in  $\text{MeOH-KOH}$ ; heating with concd.  $\text{HCl}$  gives dimethylchrysinidin chloride, the iodide forms red microneedles. The chloride, heated with  $\text{HI}$  in  $\text{PhOH}$ , gives chrysinidin iodide, bright red needles, converted by  $\text{AgCl}$  into the chloride, orange-yellow, with  $2\text{H}_2\text{O}$ , darkens  $130^\circ$ , does not m.  $300^\circ$ . The yellow concd.  $\text{H}_2\text{SO}_4$  soln. exhibits a weak green fluorescence. The color base is red; its aq.  $\text{Na}_2\text{CO}_3$  soln. is red but the color is neither intense nor persistent on diln. *Perchlorate*, orange-yellow, darkens  $178^\circ$ , m.  $185^\circ$  (decompn.).  $5,7,4'\text{-Trimethoxyflavylium chloride}$  with  $\text{HI}$  in  $\text{PhOH}$  gives the iodide, which is converted by  $\text{AgCl}$  into apigeninidin chloride, red needles with  $2\text{H}_2\text{O}$ , darkens  $180^\circ$ , does not m.  $300^\circ$ . A film on glass has a fine green luster. The orange-red  $\text{EtOH}$  soln. has a weak green fluorescence, while the yellow  $\text{H}_2\text{SO}_4$  soln. has a bright fluorescence. The color base has a port wine-red color, sol. in  $\text{Na}_2\text{CO}_3$  or  $\text{NH}_4\text{OH}$  to a rich damson soln. In  $\text{NaOH}$  the ring is easily broken and acids ppt. a chalcone, converted by mineral acids to the pyrylium salt. *Perchlorate*, orange-yellow, darkens  $190^\circ$ , softens  $220^\circ$ , decomp.  $222^\circ$ .  $2,4\text{-Dimethoxyphenyl 2-hydroxy-4,6-dimethoxystyryl ketone}$ , pale yellow, m.  $151^\circ$ , forms a red K salt and with concd.  $\text{HCl}$  gives  $5,7,2',4'\text{-tetramethoxyflavylium chloride}$ , red needles, decomp.  $134^\circ$ ; *ferrichloride*, red needles, decomp.  $180^\circ$ ; the yellow  $\text{H}_2\text{SO}_4$  soln. exhibits a green fluorescence, also characteristic of the orange-pink iso-AmOH soln.  $\text{HI}$  in  $\text{PhOH}$ , as above, gives luteoflavinidin chloride, orange-yellow needles with  $2\text{H}_2\text{O}$ , darkens  $190^\circ$ , does not m.  $300^\circ$ ; the color base is deep red and the alk. soln. reddish violet.  $5,7,3',4'\text{-Tetramethoxyflavylium chloride}$  gives rise to luteolinidin chloride, reddish brown, with  $2\text{H}_2\text{O}$ , darkens  $200^\circ$ , does not m.  $300^\circ$ ; the red  $\text{EtOH}$  solns. are devoid of fluorescence; the yellow  $\text{H}_2\text{SO}_4$  soln. has a faint green fluorescence; the aq. solns. are colored magenta, bluish violet and pure blue by  $\text{AcONa}$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{NaOH}$ , resp. The  $\text{FeCl}_3$  reaction is violet-blue in  $\text{EtOH}$ , reddish violet in  $\text{H}_2\text{O}$ .  $3,5,7\text{-Trimethoxyflavylium chloride}$  and  $\text{HI}$  give a golden brown iodide,  $\text{C}_{20}\text{H}_{11}\text{O}_4\text{IHI} \cdot 3\text{H}_2\text{O}$ , m.  $145^\circ$ , changed by  $\text{AgCl}$  to galanginidin chloride.  $7\text{-Hydroxy-3,3',4'-trimethoxyflavylium chloride}$  gives fisetinidin chloride, reddish brown, with  $0.5\text{H}_2\text{O}$ , which resembles cyanidin in its color reactions. It, however, does not melt when plunged into a bath at  $222^\circ$ ; solns. of the violet color base have a redder tinge than those of cyanidin; the blue  $\text{FeCl}_3$  color fades more rapidly; the blue alk. solns. are more unstable; the yellow-orange  $\text{H}_2\text{SO}_4$  solns. have an apple-green fluorescence which becomes dark green on standing.  $3,5,7,2',4'\text{-Pentamethoxyflavylium chloride}$ , red needles with green reflex, decomp.  $155^\circ$ ; *ferrichloride*, bright red needles, decomp.  $191^\circ$ .  $\text{HI}$  gives morinidin chloride. The blue alk. solns. of many anthocyanidins are dichroic and even if blue in thin layers or when dil. the color is bluish violet to reddish violet to red in thicker layers or in greater concn. This dichroism is especially characteristic of alk. solns. of morinidin. VII. Preparation of the anthocyanidins with the aid of  $2,4,6\text{-triaceoxybenzaldehyde}$ . *Ibid* 1152-90.— $2,4,6\text{-Triaceoxybenzaldehyde}$  (I), m.  $151^\circ$ , has 0.5 mol.  $\text{H}_2\text{O}$  not lost at  $100^\circ$ . Condensation with this in  $\text{HCO}_2\text{H}$  affords a convenient method for the prepn. of anthocyanidins.

*o*,2-Dimethoxyacetophenone (II),  $b_p$  165° (semicarbazone, m. 137°), results in 12 g. yield from 29.5 g.  $\text{MeOCH}_2\text{COCH}(\text{OMe})\text{CO}_2\text{Et}$  and 25.5 g. *o*- $\text{MeOC}_6\text{H}_4\text{COCl}$ ; the corresponding 3-deriv. (III)  $b_p$  155° (semicarbazone m. 128°). I and II in  $\text{HCO}_2\text{H}$ , treated with HCl, give *datscetinidin chloride* 3,2'-*di-Me ether*, orange-red needles, darkens 250°, does not m. 280°. HI in PhOH gives *datscetinidin chloride*, red needles with  $\text{H}_2\text{O}$ , darkens 240°, in EtOH a trace of  $\text{Na}_2\text{CO}_3$  gives a violet color which, on addn. of more  $\text{Na}_2\text{CO}_3$ , becomes more intense and duller in tone, while on diln. with  $\text{H}_2\text{O}$  the color is reddish violet. I and III give 5,7-dihydroxy-3,3'-dimethoxyflavylum chloride, deep brownish crimson, with  $\text{H}_2\text{O}$ , darkens 195°, decomp. 225°; the cherry-red EtOH soln. is rapidly decolorized by  $\text{H}_2\text{O}$ . 3,5,7,3'-Tetrahydroxyflavylum chloride, red needles, decomp. 200°. It has a remarkable faculty for passing into the pseudo-base. Aq. alk. solns. are reddish violet, while in EtOH soln. a curiously dichroic reddish blue color is produced by addn. of a trace of NaOH or excess  $\text{Na}_2\text{CO}_3$ . The salt reduces Fehling soln. and is extd. from aq. soln. by iso-AmOH. *Pelargonidin chloride* 3,3'-*di-Me ether*, from I and *p*- $\text{MeOC}_6\text{H}_4\text{COCH}_2\text{OMe}$ , intense crimson microneedles, does not m. 300°; the orange  $\text{H}_2\text{SO}_4$  soln. exhibits a green fluorescence. With  $\text{H}_2\text{O}$  or  $\text{AcONa}$  it gives the pseudo-base. The salt is extd. by iso-AmOH from aq. solns. Demethylation gives *pelargonidin chloride*. *Morinidin chloride* 3,2',4'-*tri-Me ether*, brick-red needles, darkens at 250°, does not m. 300°; the orange-red aq. solns. are decolorized on great diln. The color base is a dark mauve-crimson ppt. and the  $\text{NH}_4\text{OH}$  soln. is brick-red. The red soln. in concd.  $\text{H}_2\text{SO}_4$  has a bright green fluorescence. *Perchlorate*, crimson needles. *Cyanidin chloride* 3,3',4'-*tri-Me ether*, crimson needles with 1.5  $\text{H}_2\text{O}$ , decomp. 208°. *Delphinidin chloride* 3,3',4',5'-*tetra-Me ether*, slender needles with dark green reflex, does not m. 230°. The blue-cherry red EtOH soln. is rapidly decolorized by  $\text{H}_2\text{O}$ ; the aq.  $\text{Na}_2\text{CO}_3$  soln. has a greenish brown tinge. VIII. A new synthesis of *pelargonidin chloride* and of *galanginidin chloride*. THOMAS MALKIN AND R. ROBINSON. *Ibid* 1190-5—Bulow's process for synthesizing anthocyanidins has been investigated but, on account of the possibility that mixts. may be obtained, this method is likely to prove inferior to the other methods in use. *Phenyl  $\alpha$ -methoxy- $\beta$ -hydroxyvinyl ketone*, m. 112°, gives a brownish purple color with  $\text{FeCl}_3$  in EtOH; isolated as the *Cu salt*, m. 178°. *Phloroglucinol* and HCl give *galanginidin chloride* 3-*Me ether*, deep orange-brown, with  $\text{H}_2\text{O}$ ; this was also prepd. from 2,4,6-( $\text{AcO}$ ) $_3\text{C}_6\text{H}_2\text{CHO}$  and  $\text{BzCH}_2\text{OMe}$ . The tendency to form the pseudobase in neutral or alk. soln. is very marked. *Perchlorate*, deep brown, with a golden reflex, does not m. 300°. *Galanginidin chloride* is obtained by the action of HI. *Anisyl  $\alpha$ -methoxy- $\beta$ -hydroxyvinyl ketone*, analyzed as the *Cu salt*, pale green, m. 170°. *Pelargonidin chloride* 3,4'-*di-Me ether*, from the ketone and *phloroglucinol* with HCl, dark crimson, crystg. with  $\text{H}_2\text{O}$ . *Perchlorate*, dark crimson, m. 220° (decompn.).

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**Nitro- and aminoethoxypyridine.** J. N. COLLIE AND GERALD BISHOP. *J. Chem. Soc.* 127, 962-4 (1925); cf. *Ibid* 73, 235 (1893).—4-Ethoxy-2,6-dimethylpyridine (I), with fuming  $\text{HNO}_3$  and concd.  $\text{H}_2\text{SO}_4$  yields a nitro deriv. (II), m. 99°, slightly volatile with steam. Reduction ( $\text{Sn}$  and HCl) gives the amino deriv., m. 62°, b. 267°, absorbs  $\text{CO}_2$  from the air;  $\text{SnCl}_4$  salt,  $3(\text{C}_6\text{H}_5\text{ON}, \text{HCl}) \cdot 2\text{SnCl}_4 \cdot \text{H}_2\text{O}$ , light yellow; *chloroplatinate*, very slightly sol.;  $\text{AgNO}_3$  salt,  $\text{C}_6\text{H}_5\text{ON}, \text{AgNO}_3 \cdot 2\text{H}_2\text{O}$ . Oxidation of II gave an acid,  $\text{C}_6\text{H}_5\text{O}_2\text{N}$ , m. 147°; *Ag salt* explodes faintly on heating; the Cu, Ag, Hg, Fe and Ca salts are insol. in  $\text{H}_2\text{O}$ ; the Na and  $\text{NH}_4$  salts are easily recrystd. from  $\text{H}_2\text{O}$ . Oxidation of I gave an acid (III), crystg. with difficulty and m. 138°, whose *chloroplatinate*,  $(\text{C}_6\text{H}_5\text{O}_2\text{N}, \text{HCl})_2 \cdot \text{PtCl}_4$ , and *Ag salt* were analyzed; HI gives 4-hydroxy-2-methylpyridine-6-carboxylic acid, m. 295°, while heating alone gave an *ethoxypyridine*, b. about 220°, whose *chloroplatinate*, m. 207°. Boiling III with  $\text{HNO}_3$  gives a nitrate, m. 125°. Oxidation of I with  $\text{KMnO}_4$  gave a mixt. of 2 acids, 1 of which,  $\text{C}_6\text{H}_5\text{O}_2\text{N}$ , m. 200°; *Ag salt* and *chloroplatinate*: distn. gives  $\text{CO}_2$  and 4- $\text{EtOC}_6\text{H}_4\text{N}$ , b. 200-2° (*chloroplatinate* m. 215°). The 2nd acid, on heating, gave  $\text{CO}_2$  and 4-hydroxy-2-methylpyridine, b. 350-60°. *chloroplatinate*,  $(\text{C}_6\text{H}_5\text{ON}, \text{HCl})_2 \cdot \text{PtCl}_4 \cdot \text{H}_2\text{O}$ . C. J. W.

**Nitration of  $\alpha$ - and  $\gamma$ -aminoquinolines.** A. E. CHICHIBABIN, D. P. VITKOVSKI, AND M. I. LAFRIN. *Ber.* 58B, 803-7 (1925); cf. C. A. 15, 3108.—Nitration of  $\alpha$ -aminoquinoline (I) under the conditions which with  $\alpha$ - $\text{C}_6\text{H}_4\text{NNH}_2$  yields the nitramide,  $\text{C}_6\text{H}_4\text{N}_2\text{NNHNO}_2$ , gives  $\alpha$ -*quinolynitramide* (II), which nitrates in hot  $\text{H}_2\text{SO}_4$ , although with some difficulty, into 6-nitro-2-aminoquinoline (III) (also always formed as by-product in the prepn. of II); with  $\text{HNO}_3$ , III gives 6-nitrocarbostyryl.  $\gamma$ -Aminoquinoline (IV) under the same conditions gives a compd. (V) identical with that described by Claus and Frobenius (*J. prakt. Chem.* 56, 202 (1897)) as  $\beta'$ -nitro- $\gamma$ -aminoquinoline (VI), which is easily isomerized by  $\text{H}_2\text{SO}_4$  to a compd. (VII) oxidized by alk.  $\text{KMnO}_4$  to 5,2- $\text{O}_2\text{N}(\text{H}_2\text{N})\text{C}_6\text{H}_3\text{CO}_2\text{H}$ . V is therefore really  $\gamma$ -*quinolynitramide* and the true VI

is VII, and C. and F.'s "dinitro- $\gamma$ -aminoquinoline" is in reality 6-nitro-4-quinolynitramide. I and IV therefore behave like the analogous  $C_8H_7N$  compds. on nitration but the resulting nitramides differ from the  $C_8H_7N$  derivs. in that, on isomerization, the  $NO_2$  group migrates to the  $C_4H_4$  and not the  $C_8H_7N$  nucleus. The amination of quinoline with  $NaNH_2$  does not proceed as smoothly as that of  $C_8H_7N$ , the yield of I varying and hardly exceeding 40% under the best conditions (considerable diln. (10–20 g. quinoline in 15–20 parts xylene), careful powdering of the  $NaNH_2$  protected from moisture, and thorough stirring). II, faintly yellowish, decomps. 223–5°, reddens in the light and air, forms difficultly sol. salts with alkalis, in which it therefore dissolves easily only on warming. III, from II heated 2 hrs. at 130° in 15 parts  $H_2SO_4$ , m. 261°, insol. in dil. alkalis but easily sol. in dil. mineral acids. V, yellowish hydrated needles, decomps. 207°, insol. in dil. mineral acids but easily sol. in dil. alkalis and reprecipitated by acids. VII, from V merely dissolved in concd.  $H_2SO_4$ , yellow, m. 272° (decompn.), easily sol. in dil. mineral acids and reprecipitated by alkalis.

C. A. R.

**Synthesis of 1,2-dihydroquininaldine.** FREDERICK ALFRED MASON. *J. Chem. Soc.* 127, 1032–5 (1925).— $ClCHMeCH_2CH(OEt)_2$  (25 cc.), 50 cc.  $AmOH$ , 25 g. powd.  $K_2CO_3$ , 1 g.  $Cu$  powder, 2 g.  $NaI$  and 13 cc.  $PhNH_2$ , heated 48 hrs., give 56% of  $\beta$ -anilino- $\gamma$ -butyraldehyde diethylacetal,  $b_p$  153–4°,  $b_n$  173–5° (picrate, yellow, m. 188–90°), 10 cc. of which and 10 g.  $P_2O_5$  in 50 cc.  $C_6H_6$  give 2.2 cc. 1,2-dihydroquininaldine,  $b_p$  125–30°.  $\beta$ - $p$ -Ethoxyanilino- $\gamma$ -butyraldehyde diethylacetal,  $b_p$  190–2° (68% yield); attempts to close the ring gave an oil,  $b_p$  260–70°, whose picrate, m. 190° and  $HCl$  salt, m. 234–6°; this does not appear to be the expected  $p$ -ethoxydihydroquininaldine. Neither of the above products was found on heating  $PhNH_2$  and  $MeCH_2CH(OEt)_2$ , and neither quininaldine nor dihydroquininaldine was produced from  $PhNH_2$  and  $MeCHClCH_2CHO$ .

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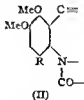
**Action of hydrogen chloride on cyclohexylidenearine and on cyclopentylidenearine.** WM. H. PERKIN, JR. AND S. G. P. PLANT. *J. Chem. Soc.* 127, 1138–41 (1925); cf. C. A. 18, 3189.—Cyclopentylidenearine, pale yellow,  $b_p$  130–2°, m. 25°;  $HCl$  in tetrahydronaphthalene gives tricyclopentylmethylenbenzene, m. 97°. 1-Methyltetraphenylpyrrole, m. 210°, insol. in dil. acids and crystals unchanged from  $Me_2SO_4$ . Cyclohexylidenecyclopentylidenearine,  $b_p$  140–5°, in poor yields from cyclopentanone and cyclohexanone hydrazone. The action of  $HCl$ , under a variety of conditions, gave only resinous products.

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**Aromatic esters of acylegonines.** WM. H. GRAY. *J. Chem. Soc.* 127, 1150–8 (1925).—The  $O$ -Me group of the tropane skeleton of cocaine (I) has been replaced by aromatic alc. residues, giving rise to substances which, in most cases, are more active anesthetics than I, as tested on the cornea of the rabbit. Benzoylcegonine (II),  $NaOH$ ,  $PhCH_2Cl$  and  $C_6H_5N$  give benzylbenzoyl- $\gamma$ -ecgonine (III), thick oil with a tropine-like odor;  $HCl$  salt m. 171° (cor.),  $[\alpha]_D^{20}$  –18.62° (2% in  $H_2O$ );  $HNO_3$  salt m. 163° (decompn.);  $H_2SO_4$  salt m. 206–8°; chloroaurate m. 111°; chloroplatinate with  $2H_2O$ , lost at 60° in vacuo m. 210°; picrate m. 80°. I and  $p$ - $O_2NC_6H_4CH_2Cl$  give the  $p$ -nitrobenzoyl deriv. (IV), oil;  $HCl$  salt, m. 178.5°, sol. in 40 parts  $H_2O$  at 15°,  $[\alpha]_D^{20}$  17.98° (2% in  $H_2O$ );  $HNO_3$  salt m. 187°;  $H_2SO_4$  salt m. 195°; chloroaurate m. 154°; chloroplatinate, crystg. with  $2.5H_2O$ , m. 210°; picrate m. 84°; attempts to reduce the  $NO_2$  group failed.  $o$ -Acetoxybenzoyl chloride  $b_p$  135°; with I this yields the  $o$ -hydroxybenzoyl deriv. (V), oil; picrate.  $\beta$ -Phenylethyl deriv. (VI) of I m. 100°;  $HCl$  salt m. 196°,  $[\alpha]_D^{20}$  –39.2° (2% in  $H_2O$ ); chloroplatinate m. 216°; picrate m. 66°.  $\alpha$ -Phenylethyl deriv. (VII), oil;  $HCl$ ,  $HBr$  and  $HNO_3$  salts are extremely deliquescent. Chloroaurate m. 170°. Phenylpropyl deriv. (VIII), oil; the  $HCl$  salt is also oily. Benzyltropoyl- $\gamma$ -ecgonine (IX), oil, by heating the product from ecgonine- $HCl$  and  $PhCH_2Cl$  with the acetylchloride of tropic acid; the  $HCl$  salt is also an oil; chloroaurate m. 90°; picrate m. 65°. Benzyl- $o$ -hydroxybenzoyl- $\gamma$ -ecgonine (X), oil; picrate m. 67°. Benzyl-2-hydroxy-3-methylbenzoyl- $\gamma$ -ecgonine (XI), oil; picrate, m. 67°. The 4-Me deriv. yields a picrate, m. 70°. Benzylbenzoyl- $\delta$ -ecgonine (XII), from benzyl- $\delta$ -ecgonine and  $Bz_2O$ , oil;  $HCl$  salt, m. 213°, sparingly sol. in  $H_2O$  at 20°;  $HNO_3$  salt m. 168°; tartrate m. 155°; mucate m. 142–3°; picrate m. 80°.  $\beta$ -Phenylethylbenzoyl- $\delta$ -ecgonine (XIII) m. 63°;  $HCl$  salt, m. 197°, sol. in 80.6 parts  $H_2O$  at 16°,  $[\alpha]_D^{20}$  35° (1% in  $H_2O$ ). The following figures represent the min. concn. effective on the cornea and by subcutaneous injection and the av. lethal dose; they are arranged in order of decreasing action on the cornea: XII, 0.05–0.025, 0.01–0.005, 39; XIII, 0.1–0.05, 0.005–0.0025, 18; VII, 0.1–0.05, 0.005–0.0025, 18; VI, 0.1–0.05, 0.01–0.005, 16.5; III, 0.1–0.05, 0.01–0.005, 33; X, 0.1–0.05, 0.01–0.05, ca. 90; VIII, 0.1, 0.1–0.05, 45.5; V, > 0.1, > 0.1, 50; I, 0.2–0.1, 0.04, 25; XI, > 0.2, 0.2–0.1, ca. 50; IV, > 0.5, 0.1–0.05, ca. 50; IX, 1.0–0.5, 0.05–0.025, ca. 40.

C. J. West

Strychnine and brucine. III. Position of the methoxy groups in brucine. FRANCIS LIONS, WM. H. PERKIN, JR., AND ROBERT ROBINSON. *J. Chem. Soc.* 127, 1158-69 (1925), cf. *C. A.* 19, 293.—Because the brucine- $\text{HNO}_3$  reaction is so characteristic, a study has been made of the behavior with  $\text{HNO}_3$  of certain synthetic compds. contg. MeO groups oriented so as to be typical of the various possibilities which must be considered in the case of brucine. The results indicate that brucine contains 2MeO groups in the *o*-position to each other in a  $\text{C}_6\text{H}_4$  ring, and the quinones from brucine and its derivs. are *o*-quinones. If brucine contains a  $\text{C}_6\text{H}_4$  ring bearing only 4 substituents, then these are arranged as in I; if the ring bears more than 4 substituents, such arrangements as II are possible. An alternative statement is that there can be no unsubstituted position in the  $\text{C}_6\text{H}_4$  nucleus *p* to either of the MeO groups.  $\beta$ -2,5-Dimethoxyaminopropenyl Me ketone, m. 55°, readily hydrolyzed by dil. acids, from 2,5-(MeO) $\text{C}_6\text{H}_3\text{NH}_2$  and  $\text{CH}_3\text{Ac}$ . Concd.  $\text{H}_2\text{SO}_4$  yields 5,8-dimethoxy-2,4-dimethylquinoline, m. 107°; *HCl* salt, yellow, m. 235-7°; picrate, yellow, m. 190°. Reduction with Na and abs. EtOH gives the 1,2,3,4-tetrahydro deriv., b<sub>10</sub> 170-2°; its *HCl* salt gives no color with cold  $\text{FeCl}_3$  but on warming a  $\text{KMnO}_4$ -color develops, fading to reddish brown. Concd.  $\text{HNO}_3$  or dil.  $\text{HNO}_3$  contg. a trace of  $\text{NaNO}_2$  gives a dark blood-red color. *N-Ac* deriv., m. 85-6° (about 60% yield); concd.  $\text{H}_2\text{SO}_4$  gives a yellowish green soln. changing to green and then to brown; on heating the color changes are through brown, reddish violet, red to orange. 6-Nitro-1-acetyl-5,8-dimethoxy-2,4-dimethyl-1,2,3,4-tetrahydroquinoline, m. 127°; reduction followed by acetylation gives the 6-acetyl amino deriv., m. 171°.  $\beta$ -6-Bromo-3,4-dimethoxyaminopropenyl Me ketone, m. 78-9°, with concd.  $\text{H}_2\text{SO}_4$  yields 8-bromo-5,6-dimethoxy-2,4-dimethylquinoline, pale yellow, m. 74-5° (70% yield); *HCl* salt, yellow, m. 136-8°; reduction gives the 1,2,3,4-tetrahydro deriv., b<sub>11</sub> 166-7°, whose *HCl* salt gives a pink, then wine-red color with  $\text{FeCl}_3$ .  $\text{NaNO}_2$  in dil.  $\text{HNO}_3$  ppt. an oily yellow-orange nitrosoamine. *Ac* deriv., oily; with  $\text{HNO}_3$  in  $\text{H}_2\text{SO}_4$  it gives an intense reddish brown color;  $\text{HNO}_3$  in AcOH gives a yellow color.  $\beta$ -3,4-Dimethoxyaminopropenyl Me ketone m. 79°. 6,7-Dimethoxy-2,4-dimethylquinoline m. 81.5-2°; *HCl* salt m. 286° (decomp.); picrate, yellow, m. 239°. The 1,2,3,4-tetrahydro deriv. m. 73-4°, b<sub>11</sub> 186-9°; picrate, Au-yellow, m. 145°. The *HCl* salt gives a pure olive-green color with  $\text{FeCl}_3$ . 1-Ac deriv. m. 118°; a trace of  $\text{HNO}_3$  in  $\text{H}_2\text{SO}_4$  gives a bright orange-red color, identical with that from brucine, though the color fades a little more rapidly.  $\text{HNO}_3$  in AcOH gives a color reaction similar to that of brucine, though the brucine reaction is exhibited at a much lower concn. of  $\text{HNO}_3$ .  $\beta$ -2,3-Dimethoxyaminopropenyl Me ketone, pale yellow oil, darkening on exposure to the air to orange-red. 7,8-Dimethoxy-2,4-dimethylquinoline b<sub>11</sub> 189-91°; *HCl* salt, pale yellow, m. 145°. 1,2,3,4-Tetrahydro deriv. b<sub>11</sub> 168-70°; *N-Ac* deriv. m. 98-9°; the AcOH soln gives no color with a little  $\text{HNO}_3$  and only a pale yellow with more  $\text{HNO}_3$ . 8-Nitro-4-allyl-veratrole, lemon, m. 44°; reduction and acetylation give the 5-acetyl amino deriv., m. 126-7°; in  $\text{H}_2\text{SO}_4$  or  $\text{HNO}_3$  it gives the characteristic brucine reaction with  $\text{HNO}_3$ . 2-Nitroveratraldehyde and  $\alpha$ -hydrindone with *HCl* give 2'-nitro-3',4'-dimethoxy-2-benzylidene-1-hydrindone, yellow, m. 156-76°, probably a mixt. of stereoisomers; the  $\text{H}_2\text{SO}_4$  soln is orange-red. Attempts to obtain a quinoline deriv. by reduction were fruitless. The corresponding 6'-nitro deriv. is brownish yellow and m. 211°; the  $\text{H}_2\text{SO}_4$  soln is bright red. Reduction gives dimethoxyindenquinoline, m. 188-90°, whose *HCl* salt, m. 251-2°, gives an intensely bluish purple fluorescent soln. in EtOH.



C. J. WEST

Abietic acid. J. FREIKA AND F. BALAS. *Spisy Přírodovědnou Fakultou Masarykovy University* 1923, No. 29, 3-12, cf. *Monatsh.* 15, 627(1894); *C. A.* 2, 108.-115 g. Na abietate prep'd. from American colophony of type I by the method of Mach was oxidized with 150 g.  $\text{KMnO}_4$  added at 0° within 48 hrs. Among the products of oxidation were iso- $\text{PrCO}_2\text{H}$  and an acid  $\text{C}_{19}\text{H}_{31}\text{O}_2$  (I), while the tetrahydroxyabietic acid of Levy could not be detected. I, m. 89-90°, amorphous, optically inactive, monobasic, difficultly sol. in boiling water, mol. wt. 178.2, was ppt'd. as its *Pb* salt from the petroleum

ether-sol. fraction of the oxidation product. The *Ag* and *Ba* salts and the oxime, m. 172°, were analyzed. MARY JACOBSEN

Dehalogenation of halogen xanthine derivatives. E. YOSHITOMI. *J. Pharm. Soc. Japan* No. 512, 839-53 (1924) ~A continuation of previous studies (C. A. 18, 3174; 19, 2303).—The catalytic reduction with alk. Pd colloid is satisfactory with 8-bromothexobromine, 8-chloroparaxanthine and 7,8-dichlorocaffeine. In the last compd., at the end of complete hydrogenation, 4 atoms of H are taken up, giving caffeine; but if 0.5 this amt. of H is used, a mixt. of caffeine and 8-chlorocaffeine is produced, showing that in this reduction, 8-chlorocaffeine must first be formed, then caffeine. By electrolytic reduction of 7,8-dichlorocaffeine for 4 hrs. in 50%  $H_2SO_4$  with Pb electrodes, both caffeine and 8-chlorocaffeine are obtained. If electrolyzed only for 2 hrs., only 8-chlorocaffeine is produced, but a longer electrolysis produces always both 8-chlorocaffeine and caffeine, and in no case is desoxycaffeine produced. Desoxytheophylline is produced from theophylline if Julius' method of electrolysis is used, as is desoxycaffeine from caffeine by the Thomas and Julius method. In order to test an idea that the reason why desoxy compds. are not formed by V.'s method of electrolysis may be due to the formation of halogen acids, theophylline was electrolyzed in 50%  $H_2SO_4$  while HCl was added drop by drop, but desoxytheophylline was not formed. Next assuming that Cl liberated may become so detrimental to the electrodes as to prevent a further reduction, 1% AcOH was added to the catholyte, but under this condition only caffeine was produced from 7,8-dichlorocaffeine. If Hg is used as a cathode, using 1.8 amp. for 4 hrs., desoxytheophylline is produced from chlorotheophylline, and desoxycaffeine from 7,8-dichlorocaffeine. Chlorotheophylline must be first reduced to theophylline and then desoxytheophylline, and similarly successive reduction must run from 7,8-dichlorocaffeine  $\rightarrow$  8-chlorocaffeine  $\rightarrow$  caffeine  $\rightarrow$  desoxycaffeine. S. T.

On the sixtieth birthday of Heinrich Biltz. ERNST WILKE-DÖRFURT. *Z. angew. Chem.* 38, 457-8 (1925).—Brief biography with portrait. E. H.

Isolation of a product of hydrolysis of the proteins hitherto undescribed (SCHRIVER, et al.) IIA. The relations between molecular constitution and color (IONESCU) 2.

Die Methoden der Organischen Chemie. Ein Handbuch für die Arbeiten im Laboratorium. Part I. Edited by J. Houben. Leipzig: Georg Thieme, 1340 pp. Price, paper R. M. 66; bound R. M. 75. Reviewed in *Chemistry & Industry* 44, 641 (1925). Cf. C. A. 19, 1575.

DONNINGTON, G. C.. A Class Book of Chemistry. Part V. Organic Chemistry, by T. M. Lowry and P. C. Austin. London: Macmillan & Co., Ltd. pages 530-708. 3s.

LOWY, ALEXANDER: Organic Type Formulas. 3rd ed. revised. New York: D. Van Nostrand Co. 6 pp. \$0.15.

LOWY, ALEXANDER: Organic Type Reactions Known by Their Originators' Names. 2nd ed. revised. New York: D. Van Nostrand Co. 6 pp. \$0.15.

Aminoalkylaminonaphthalenesulfonic acid. J. HUISMANN, W. DUTSBERG, W. HENTRICH and L. ZER. U. S. 1,543,569, June 23.  $\omega$ -Aminoalkylaminonaphthalenesulfonic acids are obtained by reacting with ethylenediamine or other aliphatic diamines in the presence of sol. salts of  $H_2SO_4$ , e. g.,  $NaHSO_4$ , upon naphthalenesulfonic acids having at least one of the reactive groups  $NH_2$  or  $OH$ , e. g., 1-naphthol-4-sulfonate of Na. The products are whitish powders generally difficultly sol. in  $H_2O$ , form alkali metal salts, are sol. in dil. inorg. acids and form characteristic cryst. colored nitroso compds. They may be used for prep. dyes.

Acids from aromatic hydrocarbons. J. F. NORRIS and E. W. FULLER. U. S. 1,542,264, June 16. In making an aromatic acid such as benzoic acid an aromatic hydrocarbon such as  $C_6H_6$  is treated with phosgene and  $AlCl_3$ . There is formed a large quantity of a compd. of  $AlCl_3$  and aromatic acid chloride and a small quantity of a compd. of  $AlCl_3$  and a diaryl ketone by conducting the reaction in the presence of a substance such as  $CS_2$  which dissolves the hydrocarbon and removes a large quantity of the reaction products from the sphere of reaction before secondary reactions occur.

Aminosalicilic acid. J. F. NORRIS and E. O. CUMMINGS. U. S. 1,542,265, June 16. Aminosalicilic acid or similar amino acids are prepd. by reduction from the corresponding aryl azo acid, by use of a  $TiCl_3$  soln.

Recovering and concentrating acetic acid. T. J. BREWSTER. Can. 247,385, Mar. 3, 1925. A diluted soln. of AcH is flowed downwardly, and ether upwardly in

intimate contact, through a column, the soln. is withdrawn at the bottom and heated to sep ether therefrom and thus ether with the ether removed from the ext. from the top of the column is returned to the lower end of the column.

Apparatus for the manufacture of acetic acid from acetaldehyde. H. W. MATHE-SON. Can. 247,519, Mar. 10, 1925.

Purifying acetone. H. F. WILLIAMS. U. S. 1,542,538, June 16. Impure acetone is treated with an acid, *e. g.*, with dil.  $\text{H}_2\text{SO}_4$ , and the treated material is subjected to distn. The first and last portions of the distillate are separately collected and the middle portion of the acetone distillate is further purified by treatment with a dil. alk.  $\text{KMnO}_4$  soln. or other oxidizing agent.

## 11—BIOLOGICAL CHEMISTRY

PAUL E. HOWE

### A—GENERAL

FRANK P. UNDERHILL

The influence of alcohol on the viscosity of blood serum. KATSUZO HAYASHI. *Kolloid-Z.* 36, 227 (1925).—When EtOH is added to blood serum of cattle the density decreases and the viscosity increases almost or altogether linearly. The viscosity increases from 1.5781 when 0.5 cc. of  $\text{H}_2\text{O}$  is added to 5 cc. of 2-day-old serum to 1.8490 when 0.5 cc. of 50% alc. is added to the same amt. of the same sample of serum. No min. as found by Fürth and Bluh was found (cf. *C. A.* 18, 1837). F. R. BROWN

Differentiation between photochemical and photodynamical phenomena. G. VIALE. *Arch. ital. biol.* 73, 19–23 (1924).—Expts. with the action of light on starch-iodide quinone-bisulfate soln. show that when the fluorescence of the system is lessened by increasing addns. of NaCl, the rapidity of the reaction is correspondingly retarded, indicating that the liberation of I is brought about through the luminescence of the system, and not through the nature of the substance added. A. T. CAMERON

The dispersion of cellular colloidal electrolytes in relation to mineral exchanges. W. MESTREZAT AND MISS M. JANET. *Bull. soc. chim. biol.* 6, 829–53 (1924); cf. *C. A.* 18, 3605.—Expts. in which soap or gelatin solns. contg. NaCl are dialyzed through collodion membranes against NaCl solns. show that the unequal partition of electrolytes between colloid and aq. phases is detd. by the state of dispersion of the colloid and bears a direct relation to it, being max. for solns. of max. viscosity, indicating that there is an interdependence between colloids and mineral constituents. A. T. CAMERON

Evolution of our knowledge of the chemical structure of proteins. A. BLANCHETIERRE. *Bull. soc. chim. biol.* 7, 218–330 (1925).—A very complete review. A. T. C.

Energy of growth. III. Comparison of energy output in the development of molds on different organic nutrients and specific dynamic action. R. F. TERROINE, MISS S. TRAUTMANN, R. BONNET, AND R. JACQUOT. *Bull. soc. chim. biol.* 7, 351–79 (1925); cf. *C. A.* 18, 3195.—In the development of *Sterigmatocystis nigra* and *Aspergillus oryzae* the energy balance can be detd. to within 5%. The development of the mycelium, in which formation of cellulose predominates, at the expense of glucose as sole org. nutrient yields an energy output of 58%; if the sole org. nutrient be gelatin or peptone, the yield is only 39%. This difference corresponds to that observed by Terroine, Bonnet, and Joessel (*C. A.* 18, 3195) in the germination of purely amylaceous seeds and of seeds with a protein reserve, and leads to the conclusion that in all living cells formation of carbohydrates from other carbohydrates entails extremely slight loss of energy, and from proteins much greater loss. Use of glycine, alanine, asparagine, valine, leucine or glutamic acid or glucosamine-HCl as sole org. nutrient gives the same energy output as protein, 39%. The sp. dynamic action of proteins in homeotherms can be considered as a loss of energy strictly limited to de-amination, the cell utilizing the ternary chains resulting without a preliminary transformation to glucose. A. T. CAMERON

The alteration of tryptic activity of pancreas extracts depending on their method of preparation. A. N. ANOVA, A. P. PROROKAYCHENSKI AND E. A. SWESCHNIKOWA. *Fermentforschung* 8, 167–76 (1925).—Exts. were prepd. from fresh hog pancreas, before and after autolysis, by means of  $\text{H}_2\text{O}$ , 0.9% NaCl soln. and 50% glycerol, resp., and their activity toward egg albumin, gelatin, fibrin and casein was detd. The 50% glycerol ext. digests albumin and fibrin less readily than the  $\text{H}_2\text{O}$  and NaCl exts. A 1% glycerol ext. digests gelatin less readily and a 50% glycerol ext. much more readily than the aq. and NaCl exts. The 1% glycerol ext. and the aq. and NaCl exts. digest casein equally

well. Albumin, gelatin and casein are digested equally well by the aq. and NaCl exts. Autolysis of the glands increases the activity of the exts. toward all 4 proteins. This effect is more marked with fibrin and casein than with albumin and gelatin, and more dependent on the duration of autolysis. The difference in trypsin content of the various exts. is due apparently to the influence of the solvent on the activity of the enzyme rather than to variations in the completeness of extn. A. W. DOX

**Phylloerythrin.** II. Remarks on the paper of Dr. Kémeri "A new porphyrin-like constituent of normal human feces." H. FISCHER and HANS HILMER. *Z. physiol. Chem.* 143, 1-8(1925); cf. C. A. 10, 912; Kémeri, C. A. 19, 2212.—The porphyrin described by Kémeri is believed to be identical with phylloerythrin. The spectroscopic behavior and complex-salt formation show that it is probably a porphyrin. This point is of great importance, since the chlorophyll-porphyrins have hitherto been obtained only by drastic disintegration of chlorophyll, whereas phylloerythrin is formed from chlorophyll by a biological process in the organism. With the exception of mesoporphyrin no blood pigment porphyrins in Et<sub>2</sub>O show an absorption band in the red at the location of that observed with phylloerythrin and Kémeri's porphyrin. The failure to increase the phylloerythrin content of feces by a diet rich in chlorophyll, and its occurrence during a meat diet suggest that phylloerythrin is stored by the liver and gradually eliminated with the bile. Examn. of the bone marrow from a patient who died of pernicious anemia showed the presence of Kämmerer's porphyrin and coproporphyrin. This observation points to the possibility that in the synthesis of blood pigment the Fe is not introduced at this stage. A. W. DOX

**Enzymes.** L. ROSENTHALER. *Pharm. Zentralhalle* 66, 305-10(1925).—A discussion of the nature and action of enzymes as conceived by the "Munich" and "Zurich" schools. W. O. E.

**The constitution of aqueous solutions of  $\alpha$ -benzoic acid sulfamide (saccharin) and *p*-phenetyl urea (dulcin).** KURT TÄUFEL and CARL WAGNER. *Ber.* 58B, 909-12 (1925).—An attempt was made to find a relation between degree of sweetness and degree of dissociation or of hydration. Saccharin is an acid, and since its Cl, CH<sub>3</sub>, or CH<sub>2</sub>COOH derivs. are not sweet, its sweetness was ascribed to its anion. The Na salt is sweet, but is also a strong electrolyte. Attempts to depress its dissociation with Na<sub>2</sub>SO<sub>4</sub>, NaOAc, or dil. HCl did not affect sweetness within exptl. error (25%). Strong HCl interfered with the detn. of sweetness (by taste). Dulcin was found to be an extremely weak base, and its sweetness was ascribed to the free mol. The increase in sweetness on mixing saccharin and dulcin solns. is not due to salt formation, but to their relatively greater sweetness in lower concns. A. W. FRANCIS

**Further studies on the nature of polypeptide-splitting enzymes.** S. TAMURA. *Acta Schol. Med. Univ. Imp. Kioto* [IV], 6, 441-7(1924).—Optically active amino acids (particularly *D*-alanine) retard the rate of enzymic hydrolysis of glycyl-*L*-tyrosine. Neither glycocoll nor *DL*- nor *D*-lactic acid exerts any sp. influence on the reaction rate. W. F. GORDEL

**Glutathione.** Relation between the tissues and the oxidized dipeptide. H. E. TUNNICLIFFE. *Biochem. J.* 19, 199-206(1925).—Linolenic acid is not the substance in the thermostable residue responsible for the reduction of oxidized glutathione (see Meyerhof, *Arch. ges. Physiol. (Pflüger's)* 199, 531(1923)). The reduction of methylene blue by tissues proceeds more rapidly in alk. than in acid solns. BENJAMIN HARROW

**Isolation of a product of hydrolysis of the proteins hitherto undescribed.** S. B. SCHRYVER, H. W. BUSTON, and D. H. MURKHERJEE. *Proc. Roy. Soc. London* 98B, 58-65(1925).—Dry purified isinglass (gelatin) from the swim-bladder of sturgeon was thrown into boiling 25% H<sub>2</sub>SO<sub>4</sub> and subjected to hydrolysis. Then the dicarboxylic acids were pptd. as their Ba salts in the presence of alc.; and the other amino acids were sepd. as the Ba salts of their carbamates. The insol. Ba carbamate fraction, on decomposition by boiling water, yielded glycine, and a base which was pptd. by phosphotungstic acid in the presence of 5% H<sub>2</sub>SO<sub>4</sub>. This ppt. was decomposed by Ba(OH)<sub>2</sub>; the liberated base was purified by conversion into its Hg salt, then set free by H<sub>2</sub>S. The base was finally obtained as a hygroscopic solid, which absorbed CO<sub>2</sub> from the air, decomposed on melting, and was quite sol. in water, and insol. in almost all org. solvents. Its salts were usually sol. in water. The base yields a tri-Bz compd.; it contains 2 NH<sub>2</sub> groups (shown by its reaction with HNO<sub>2</sub>), and a COOH group (shown by the formal titration); its reactions, elementary compn. (% of C, H, and N), and mol. wt. (i. p. method with water as solvent) indicate it to be a hydroxylysine. Failure to form a lactone indicates the probable formula to be H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH(OH)CH(NH<sub>2</sub>)COOH. The product obtained was optically inactive, probably as a result of racemization during prepn. Hydroxylysine does not occur in casein or ovalbumin; a small trace is

present in horse blood fibrin. Other proteins contain the following amts., the hydroxylsine N being expressed in % of the total protein N:—gelatin <0.3, fish gelatin (from cod and ling skin) 1.8 to 2.2, isinglass (sturgeon swim bladder) 2.98 to 3.3, edestin 3.28, cabbage leaf albumin 1.55, alk.-sol protein of oats 1.50. JOS. S. HERBERT

The influence of various kinds of proteins on the composition of the duodenal juice. M. VON LEMEŠIC. *Wiener Arch. inn. Med.* 9, 401-S(1925).—Proteins from meat cause a higher acidity in the duodenal juice than milk or plant proteins. In general, the acidity of the duodenal contents is dependent on the degree of acidity in the stomach. The content of the duodenal juice in enzymes is greatest with meat proteins, and less with milk and plant proteins though higher than with carbohydrates, fats and milk.

HARRIET F. HOLMES

The behavior of intravenously injected trypan red in man and dog, under the influence of acids and alkalis. E. GOLDBERG and R. SEYDERHELM. *Z. ges. exp. Med.* 45, 154-66(1925).—Elimination of the acid dye trypan red in man proceeds uniformly if there is no change in reaction of the urine but if the urine becomes acid much more dyestuff is eliminated and if alk. very little. In dogs simultaneous intravenous injections of acid or alk. solns. do not alter the secretion of trypan red, indicating that the process of elimination is independent of the reaction of the blood, but a change in the inner reaction of the kidney cells alters their permeability to the dye. H. F. H.

Ethylene peroxides. The oxygenase of the Chodat-Bach system. ORDOLIO FERNÁNDEZ. *Anales soc. españ. fis. quim.* 23, 181-5(1925).—The unstable peroxides formed by ethylene comds. by addn of O at the double bond can react as oxygenases in the Chodat-Bach system. They possibly play the same role in the plant and animal organism. More or less stable peroxides of drying and semi-drying oils, anise and clove oil, ovoidicthin, Et cinnamate, benzilidene acetone and benzilidene acetophenone were prepd by heating with concd.  $H_2O_2$  (perhydrol) not over 80°. The oxygenase reactions were more or less pronounced.

MARY JACOBSEN

The photosynthetic theory of the origin of life and the production of organized forms from metaformaldehyde. A. L. HERRERA. *Atti accad. Lincei* [6], 1, 5-8(1925).—The formation of cell-like structures which consist of metaformaldehyde and traces of  $SiO_2$  and stain with aniline dyes and ferri-hematoxylin was observed in an expt. in which  $CH_2O$  was used for hardening figures obtained by gas injection into glycerolated gelatin. The colloidal  $SiO_2$  probably plays the role of a negative catalyst, preventing the complete crystn. of metaformaldehyde. The expts. demonstrate the possibility of production of cell structures, in absence of complicated org. substances, from an inorg. colloid and the primitive  $CH_2O$ , which is formed by a natural photosynthetic process. The latter probably occurred on a much larger scale in the Paleozoic epoch with its abundance of ultra-violet light (Baudisch, Church, Allen). The cells can perhaps be endowed with life by the action of Fe, Mg, formaldoxime and the reduction of nitrites and nitrates (Baly).

MARY JACOBSEN

Experimental electroendosmotic studies on living human skin. HERMANN REIN. *Z. Biol.* 81, 125-40(1924).—The rate of electroendosmosis of various solns. depends on (1) the condition of the skin (it is less in atrophied skin and rapidly decreases with death); (2) the nature of the soln. (EtOH and sucrose solns.  $>H_2O >$  neutral salt solns.) The effect increases with the concn. Hydroxyl ion always increases the flow. The inhibitory effect of cations shows the series  $K < Na < Ca < Al$ . The effect of the anions is not so regular. Chloride ion effects greatest retardation and sulfate and phosphate ions effect the least retardation.

FRANCES KRAHOW

Viscosity of blood corpuscle suspensions. I. L. BERZELLER and H. WASTL. *Biochem. Z.* 153, 110-9(1924).—Blood corpuscles were centrifuged, the plasma was removed, and the viscosity of the corpuscles at various dilns. detd. W. D. LANGLEY

Investigations of electrolyte-free, water-soluble proteins. III. Salt-protein compounds (zinc chloride). W. PAULI and MARGARETE SCHÖN. *Biochem. Z.* 153, 253-84(1924). (cf. C. A. 19, 1431).—Merck's pure  $ZnCl_2$  was dissolved in  $H_2O$ , filtered, and the sp. cond.  $K$  of a 0.1% soln. was found to remain practically const. at  $18.88 \times 10^{-4}$  for 1 yr.  $K$  values at various dilns. were detd. The H-ion concn. was detd. by the Poggendorf compensation method, and the Cl ion concn. by the calomel electrode (an isophoretic soln. of  $NH_4NO_3$  and  $NaNO_3$  being used in place of KCl). The mobility  $\mu_{25}$  decreased from 57.25 to 54.09 as the concn. decreased from  $58.05 \times 10^{-3}$  to  $2.32 \times 10^{-3}$  N. Pure serum albumin was prepd. by electrodialysis of horse serum and the sp. cond. of 0.8% and 1.06% albumin solns. with varying quantities of  $ZnCl_2$  was detd. (cf. C. A. 19, 1431). The solns. behave as though  $2.42 \times 10^{-4}$  equiv. of salt disappears per g. of protein present. The Cl value changed from  $38.7 \times 10^{-4}$  to  $4.84 \times 10^{-4}$  N.

It seems that Zn salts of albumin resemble the Ag and alkali salts, but not the Fe, Cr, and  $\text{UO}_2$  salts. With a given salt mixt. the absolute amt. of Cl bound increased as the protein increased, but the relation was not linear. Between  $\text{ZnCl}_2$  concns.  $2 \times 10^{-3}$  and  $8 \times 10^{-3} N$   $\mu_2$  was greater than was expected, and it is within this range that  $\text{ZnCl}_2$  markedly protects albumin against coagulation by heat. Protein always migrated to both electrodes, but the concn. of negative particles was relatively small. From the max. quantity of Cl bound by albumin, it was estd. that the mol. wt. of albumin is 5345. The temp. of flocculation of serum albumin with varying quantities of  $\text{ZnCl}_2$  as well as the extent of flocculation with varying quantities of  $\text{ZnCl}_2$  at const. temp. were detd. Electrolyzed gelatin (glutin) and ovalbumin were studied in the same way as serum albumin. A theoretical discussion of the mechanism for the union of  $\text{ZnCl}_2$  with proteins then follows. W. D. LANGLEY

The manner of action of thrombin. E. WÖHLISCH. *Biochem. Z.* 153, 456-8 (1924); cf. C. A. 19, 84.—Thrombin in 0.85% NaCl soln. placed on one side of a membrane impermeable to the thrombin was not able to ppt. fibrinogen as fibrin on the other. W. D. LANGLEY

The pigment transformation in living organisms. I. The change of chlorophyll under the influence of gastric juice. M. W. KORTSCHAGIN. *Biochem. Z.* 153, 510-6 (1924).—After chlorophyll in a gelatin soln. has been acted upon by gastric juice (from dogs) for 3-12 hrs., no pheophorbide is formed, although, from the spectral changes observed, it is concluded that the Mg has been split off, and that pheophytin is formed. W. D. LANGLEY

Iodine studies. I. The avidity of the thyroid gland for various iodine compounds in vitro. I. M. RABINOWITCH, with the assistance of A. B. FRITH. *J. Clin. Invest.* 1, 473-81 (1925).—Normal thyroid glands, when exposed to various dil. I solns. (Lugol's, acid iodide, KI), absorb considerably more I than other tissues. Pathol. thyroids absorb much more I than normal thyroids. The quantity of I absorbed varies with the nature of the I soln. The I taken up by the thyroid tissue does not combine with the lipid material because extn. with  $\text{CHCl}_3$  has no significant effect upon the I content. Adsorption cannot explain the phenomenon. LOUIS LEITER

A program of physiological chemistry. A. DE AGUIAR. *Rev. quim. pura aplicada* [3], 1, 85-96 (1924).—Captions and brief outlines of 40 lectures and 40 lab. expts. for medical students. M. R. SOULÉ

Action of saliva on starch. K. HATTORI. *J. Pharm. Soc. Japan* No. 516, 170-84 (1925).—Velocity consts. of the action of different concns. of saliva were detd. for 2 samples of potato starch and 2 of rice starch. Percent of  $\text{H}_2\text{O}$ , amylose, impurity and no. of cc. 0.01  $N \text{H}_2\text{SO}_4$  required to neutralize 1 g. of each starch, resp., were: 13.218, 15.940, 12.350, 7.210; 85.880, 82.125, 85.880, 90.720; 0.910, 1.935, 1.770, 2.070; 0.943, 3.770, 3.300 and 3.300. Saliva was collected daily at 11 a.m., dild. to a definite vol. and filtered. The starch was used in such quantity as to contain 1 g. amylose per final 100 cc. Digestion was conducted for exactly 30 min. in a medium contg. 5 cc.  $M \text{NaCl}$ , 2.5 cc.  $M/50 \text{Na}_2\text{HPO}_4$  and varying amts. of dild. saliva (0.2 to 1.0 cc.). The sugar was detd. by the Fehling method. The results are given in 14 figures and 2 tables. Velocity consts. vary with the different starches, but with potato starch, the velocity  $\times$  concn. is fairly const. when less than 0.5 cc. of dild. saliva is used. The fact that in rice starch this relation does not hold is explained by an assumption that rice starch may be more nearly related to dextrin, because the velocity const. of salivary digestion with rice starch is generally higher than with potato starch. In general, the action of saliva on starch follows the reaction expressed by  $dx/dt = kx(a-x)$ , where  $a$  is concn. of saliva. S. T.

Mutarotation as a factor in the kinetics of invertase action. J. M. NELSON AND OSCAR BODANSKY. *J. Am. Chem. Soc.* 47, 1624-38 (1925).—A method is described for detn. of the effect of the invert sugar on the rate of hydrolysis at any point in the course of the reaction. Invert sugar has a different retarding effect upon the rate of hydrolysis according to whether it is in a freshly liberated or in a final mutarotated form. In other words, if the invert sugar were mutarotated immediately upon its liberation, the course of the hydrolysis followed would be different from the ordinary, observed course of the reaction. If the hydrolysis of a 10% sucrose soln. is considered to consist of 2 simultaneous and continuous reactions, namely, the hydrolysis of the sucrose present and the mutarotation of the invert sugar which is being formed, a change in the relative rates of these 2 reactions has no apparent effect upon the form of the course of the hydrolysis. By comparing the actual and mutarotated hydrolysis of 8, 10 and 12% sucrose solns., it is found that in the portion of the hydrolysis where the sucrose concn. is greater than 4-5 g., the retardation of the "nascent" invert sugar is less than

that of the mutarotated, while where the sucrose concn. is less than 4-5 g., the retardation of the nascent invert sugar is greater than that of the mutarotated. C. J. WEST

Influence of tryptophan and other amino acids upon the stability and enzymic activity of pancreatic amylase. H. C. SHERMAN, M. L. CALDWELL and N. M. NAYLOR. *J. Am. Chem. Soc.* 47, 1702-9(1925).—Pancreatic amylase in pure  $H_2O$  at  $10^\circ$  lost about  $1/4$  of its activity in 4 hrs. and about 0.5 in 24 hrs. At  $25^\circ$  it lost nearly 0.5 of its activity in 2 hrs. and about  $2/3$  in 4 hrs. At  $40^\circ$  the activity was entirely lost within 1 hr. In  $H_2O$  contg. optimum concns. of NaCl and  $Na_2HPO_4$  and brought to optimum H-ion concn., the rate of inactivation was reduced to that observed in pure  $H_2O$ . Both in the presence and in the absence of salts the temp. coeff. of the inactivation of the enzyme is much higher than that of most chem. reactions. These statements apply to both the amylolytic and saccharogenic activities of the enzymes, and support the view that the inactivation of the enzyme in soln. is, at least in part, due to hydrolysis and certainly is greatly accelerated by heat. The addn. of  $NH_3$  acids to the salt soln. of the enzyme protects the enzyme from inactivation both in the absence and in the presence of its substrate. If the enzyme is a protein compd., its hydrolysis must yield  $NH_3$  acids; addn. of such acids to the soln. tends to check the hydrolysis and thus conserve its activity. Certain differences in the effect of different  $NH_3$  acids are shown to be quant. rather than qual. and are probably due to differences in the position or mode of linkages of the corresponding  $NH_3$  acid radicals in the enzyme mol. Tryptophan does not show its full effects in 30 min. at  $40^\circ$  but does so in expts. of longer duration at  $40^\circ$  or in 30 min. at  $50^\circ$ . That malt amylase is also of protein nature is also probable. C. J. WEST

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## B—METHODS AND APPARATUS

STANLEY E. BENEDICT

Porphyrias and their detection. F. UTZ. *Schweis. Apoth. Ztg.* 62, 561-3, 585-7 (1924); cf. C. A. 18, 3397.—For detection of porphyrin in feces, the method of Fischer and Schneller (C. A. 18, 1679) is recommended. S. WALDBOTT

Some observations on the reducing power of glucose in presence of copper salts in an alkaline medium (Fehling solution) and in an acid medium (Barfoed solution). P. FLEURY and P. TAVERNIER. *Bull. soc. chim. biol.* 7, 331-5(1925).—Factors such as the concn. of Cu, presence of chlorides, mannitol, etc., retard the reduction of glucose in acid soln., but produce little or no effect in alk. soln. Since the reducing power of lactose is less than that of glucose, the exaggeration of this difference involved in the use of Barfoed's reagent becomes only a particular case of a general phenomenon. A. T. CAMERON

Correction to the memoir of P. Thomas on a new reaction of pentoses. G. BERTRAND. *Bull. soc. chim. biol.* 7, 436-9(1925); cf. Thomas, C. A. 19, 1872 and Thomas and Beraru, C. A. 19, 1256. Apropos of the naphthol reaction for free and combined pentoses of Pierre Thomas. G. DENIGÈS. *Ibid.* 440-2.—Priority claims. A. T. CAMERON

Oxidation of uric acid in alkaline medium. Present state of the question. L. PIAUX. *Bull. soc. chim. biol.* 7, 443-51(1925); cf. C. A. 18, 1273.—A review. A. T. C.

Newer methods for the determination of pregnancy. ROSS MITCHELL. *Can. Med. Assoc. J.* 15, 489-93(1925).—A review, chiefly dealing with biochem. methods. A. T. CAMERON

Measurement of the real acidity of urine by means of the  $p_H$ . P. FLEURY. *Union pharm.* (April 15, 1925); *Répert. pharm.* 36, 135-7.—P. recommends the following indicator first proposed by Ch. O. Guillaumin for detg. the  $p_H$  or real acidity of urine: Triturate in a mortar 0.125 g. of methyl red, 0.40 g. of bromothymol blue and 19 cc. of 0.05 N NaOH and finally add distd.  $H_2O$  to make 1 l. To make the detn. use the urine as voided if d. = less than 1.010; if greater, dil. with  $1/10$  to  $1/5$  of neutral distd.  $H_2O$ . To 10 cc. of the sample thus prepd. add 0.5 cc. of the reagent, mix and observe the color against a white background. From the color observed, the  $p_H$  is calcd. by means of the following data: grenadine red  $p_H$  4.6, shrimp rose 5.0, yellow rose 5.4, champagne yellow 5.8, sea green 6.2, greens intermediate between sea green and vegetable green 6.6-7.0, vegetable green 7.4. The  $p_H$  of urine varies depending upon a no. of factors, especially the diet. On a mixed diet, it oscillates between 5.8 and 6.0, descending to 5.2 on a meat diet and ascending to 6.5 on a strict vegetable diet. A. G. DUMER

Micro-estimation of acetone in urine. M. MOUSSERON. *Répért. pharm.* 36, 137-8(1925).—The method of Lax (C. A. 16, 942) has been found to be accurate.

A. G. DuMEZ

Some observations on Folin and Wu's method of blood analysis. O. LATHAM. *Med. J. Australia* 1924, Suppl. 412-7; *Australian Sci. Abstracts* 3, 36.—L. deals with colorimetric methods for estg. certain biochem. ingredients of the blood and cerebrospinal fluid used by Folin and Wu's school. He is in agreement with their normal findings and praises Pyrex glass. The local difficulties of obtaining pure reagents, jack beans, etc., and methods for overcoming these are touched on. Colored glasses for estg. hemoglobin and a simple but effective home-made colorimeter are described. The nonprotein N, urea N, creatinine, uric acid, glucose and  $\text{CO}_2$  coeff. were estd. in some mental patients. But departures from the normal followed phys. rather than mental disabilities.

II. G.

An electrolytic modification of the Gutzeit method for the determination of arsenic in body tissues. W. E. LAWSON AND W. O. SCOTT. *J. Biol. Chem.* 64, 23-8(1925).—The tissue is oxidized with  $\text{H}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$  and  $\text{CuSO}_4$ . After the addition of  $\text{SnCl}_2$ , the dild. acid liquid is submitted to electrolysis, with a current of 0.0 amp. at 5 volts. The Pt anode is sepd. from the Pb cathode by means of a porous cup. The evolved  $\text{H}_2$ , etc., passes through a tube containing  $\text{Pb}(\text{OAc})_2$ -paper before reaching the  $\text{HgBr}_2$ -paper. Amts. as low as 0.002 mg  $\text{As}_2\text{O}_3$  added per g. of tissue were quant. recovered.

I. GREENWALD

A method of obtaining from veins blood similar to arterial blood in gaseous content. SAMUEL GOLDSCHMIDT AND A. B. LIGHT. *J. Biol. Chem.* 64, 53-8(1925).—The hand and wrist, to a depth of 3 in. above the radial styloid, are immersed in  $\text{H}_2\text{O}$  at  $45-47^\circ$  for 10 min. The hand is then withdrawn far enough to permit of the insertion of a needle pointed downwards into one of the veins on the back of the hand. Blood drawn under oil in this manner gave values for  $\text{O}_2$  content and capacity and for  $\text{CO}_2$  content that were almost identical with those obtained from blood drawn by arterial puncture from the same individuals.

I. GREENWALD

A simple method for obtaining cutaneous (capillary) blood from infants and adults for colorimetric  $\text{pH}$  determination. PAUL DRUCKER AND G. E. CULLEN. *J. Biol. Chem.* 64, 221-7(1925).—*Infants*.—The entire foot is placed in  $\text{H}_2\text{O}$  at  $45-50^\circ$  until a good hyperemia is produced and is then dried with  $\text{Et}_2\text{O}$ . The heel is then dipped into a funnel, about 55 mm. in diam., closed at the bottom and filled with paraffin oil, sp. gr. about 0.885. A stab wound, 5 mm. deep, is made with a 2 mm. cataract knife. The blood is allowed to drop through the oil until enough has been collected. For detns. of  $\text{pH}$ , 0.4 cc. are pipetted, under oil, into each of 2 tubes contg. 5 cc. 0.9%  $\text{NaCl}$ , one of which contains indicator. After centrifuging in closed tubes, the detn. is completed as previously described (C. A. 16, 2700). *Adults*.—The lobe of the ear or the tip of the finger is cleaned with  $\text{Et}_2\text{O}$ , dried and stabbed under oil. The correction for temp. is the same for children as for adults, but must be increased by 0.03 to allow for the loss of  $\text{CO}_2$  from the blood while dropping through the oil.

I. GREENWALD

The determination of small amounts of protein nitrogen. EDNA RUTH MAIN AND A. P. LOCKE. *J. Biol. Chem.* 64, 75-80(1925).—The method of Folin and Denis (C. A. 10, 2900) is modified by the use of a spectrometer for the detn. of the amt. of  $\text{NH}_2$ -Hg compd. formed. Amts. as small as 0.015 mg. N may be detd. with an error not exceeding 10%.

I. GREENWALD

The determination of uric acid in the blood. S. R. BENEDICT. *J. Biol. Chem.* 64, 215-9(1925).—The work of Bulmer, Eagles and Hunter (C. A. 19, 1437) shows that, in cases of Ni rash, the blood contains considerable quantities of a substance which reacts with uric acid reagents, yet is not uric acid. But the direct method of Benedict (C. A. 16, 2587) is not, therefore, to be discarded. It is so much more convenient than pptn. methods that it is the method of choice for routine detns. High values, in the absence of nephritis or other known cause, should be checked by a pptn. method. The substance reacting like uric acid is pptd. by Ag lactate, contrary to the statement of B., E., and H., but the Ag compd. is not decompd. by the acid  $\text{NaCl}$  employed. B. has isolated the substance resembling uric acid. Description is reserved.

I. G.

Modification of Bloor's method for the determination of cholesterol in whole blood or blood serum. G. E. SACKETT. *J. Biol. Chem.* 64, 203-5(1925).—Bloor's method (C. A. 10, 1656) is modified by the use of only 0.2 cc. of blood or serum, which is run into a 15 cc. centrifuge tube contg. 9 cc.  $\text{EtOH}$  and 3 cc.  $\text{Et}_2\text{O}$ . Extn. is not accelerated by heating but by placing the stoppered tube on its side for 30 min. After centrifuging, the  $\text{EtOH}$ - $\text{Et}_2\text{O}$  soln. is evapd., extd. with  $\text{CHCl}_3$ , etc. Freedom from the brown color

sometimes obtained with Bloor's method, good recovery of added cholesterol and good agreement with results obtained by Bloor's method are claimed. I. GREENWALD.

The determination of blood sugar. S. R. BENEDICT. *J. Biol. Chem.*, **64**, 207-13 (1925).—The picric acid method gives as low values for the concn. of sugar in blood as does the Folin-Wu method, provided that the tungstic acid filtrate, concd, to permit of accurate detns., is also used for the former. This indicates the presence, in blood, of some reducing substance which is pptd. by tungstic acid but not by picric acid. B. has devised a Cu reagent which, when applied to urine, gives values almost as low as those obtained by the Folin-Wu method, after treatment with Lloyd's reagent. The reagent is recommended for the detn. of blood sugar. Two cc. of the 1:10 tungstic acid filtrate are measured into a Folin-Wu sugar tube, 2 cc. of Cu reagent are added and the mixt. is heated in boiling  $H_2O$  for 4 or 5 min. After cooling, 2 cc. of the arseno tungstate reagent are added and, after 5 or 10 min., the mixt. is dild. to the mark and compared with the standards similarly prepd. from 0.2 and 0.4 mg. glucose. (An ordinary graduated test tube may be used, if 2 or 3 drops of PhH are added before the heating. The heavy PhH vapors displace the air but, on cooling, are not themselves displaced by air at the bottom of the tube.) The Cu reagent is prepd. by dissolving 200 g. Na citrate, 50 g.  $Na_2CO_3$  (anhyd.) and 1 g.  $NaHSO_4$  in 850 cc.  $H_2O$  and 6.5 g.  $CuSO_4 \cdot 5H_2O$  in 100 cc.  $H_2O$ , mixing the 2 and dilg. to 1000 cc. The  $NaHSO_4$  increases the amt. of  $CuO$  formed per mg. of sugar present. The color reagent is prepd. by dissolving 100 g. pure  $Na_2WO_4 \cdot 2H_2O$  in 600 cc.  $H_2O$ , adding 50 g.  $As_2O_3$ , 25 cc. 85%  $H_3PO_4$  and 20 cc. concd. HCl and boiling 20 min. After cooling, 50 cc. com. formalin are added and the mixt. is dild. to 1000 cc. Added glucose is recovered. The results are generally from 10 to 20% lower than those obtained by the Folin-Wu method, the normal fasting blood sugar concn. being about 75 mg. per 100 cc. B. believes that even this is too high and that the true glucose content is not over 60 mg. per 100 cc. I. GREENWALD.

Dialysis of the circulating blood in the living animal. GEORG HAAS. *Klin. Wochschr.* **2**, 1888 (1923), 4, 13-4 (1925).—The earlier communication contains a brief description of a dialysis procedure, the only objection to which appears to be the toxicity of the hirudin that is required to prevent coagulation of the blood. Non-toxic hirudin is now obtainable, hence the method, which seems to be very similar to that of J. Abel, can now be applied to man. MILTON HANKE.

Sahlb's method for estimating free acid in gastric juice by titrating the indicator solution using methyl violet as indicator. H. E. BÜTNER. *Klin. Wochschr.* **4**, 877-8 (1925).—Ten cc. of gastric contents and 10 cc. of  $H_2O$  are separately treated with 0.2 cc. of a methyl violet soln. 0.1 N HCl is then added to the aq. soln. until its color matches that of the gastric juice. Values are expressed in cc. 0.1 N acid per 100 cc. gastric juice. The values are approx. 50% as high as those obtained by the usual procedure, but they are unquestionably more truthful. Method and comparator are described in detail. Total acid is obtained by titrating with 0.1 N NaOH, with  $\alpha$ -naphtholpthalein as indicator. MILTON HANKE.

Preparation of standards for the colorimetric determination of trypsin. I. A. SMORODINTZEV AND A. N. ADOVA. *Biochem. Z.* **153**, 14-8 (1924).—Fibrin is minced, washed thoroughly, and stained with diphenylrosaniline in glycerol. The colored fibrin in known amts. is acted upon by a pancreatin prepn. and from the intensity of the color of the resulting soln. the amt. of trypsin in the pancreatin is indicated. W. D. L.

The microdetermination of blood sugar. C. J. DIAZ AND B. SANCHEZ CUENCA. *Biochem. Z.* **153**, 97-9 (1924).—The Hagador-Jensen method is good if one follows the original directions and uses pipets, but is not reliable if filter paper is used to hold the blood sample. The cause of the low and variable results with the filter paper is the rapid coagulation of the blood in contact with the  $Zn(OH)_2$  used, and a consequent impermeability of the clot when the sugar is extd. W. D. LANGLEY.

Glycolysis. H. J. JOHN. *Ann. Clin. Med.* **3**, 667-96 (1925).—A definite and uniform glycolysis takes place in blood *in vitro*. The cause is unknown. It is less in diabetic blood. It is less at icebox than at room temp. Hence samples of blood for sugar detn. should not be kept long.

The estimation of urea in the blood by the hypobromite method. F. S. FOW-WEATHER. *J. Path. Bact.* **28**, 165-9 (1925).—The technique is given in detail. The method is accurate enough for clinical purposes. JOHN T. MYERS.

Interfering substances in the testing of urine for albumin with Tanret reagent. A. DE AGUIAR. *Rev. quim. pura aplicada* [3], **1**, 202-10 (1924).—The character of the ppt. is very significant. A flocculent ppt. insol. in hot  $H_2O$  and  $C_2H_5OH$  is proteins. A flocculent ppt. sol. in those two substances may be peptones, albuminoses or quinine. A fine ppt. sol. in these solvents is urotropine. M. H. SOULE.

Notes on Burmann's glycometer. J. BURMANN. *Schweiz. Apoth. Ztg.* 63, 60-70; K. SEILER. *Ibid* 70-2(1925).—B. claims his app. to be sufficiently accurate for clinical tests. S. rejoins with a graph showing the % of difference in result caused by 1 drop of sugar solns. varying from 0.5 to 10%. His previous results (*C. A.* 18, 2944) are confirmed. Of 162 samples of urine examd. by S. for sugar, 25 showed 0-0.5%, 105, 0.5-5%; 22, 5-6% and 10, 6-9% sugar. S. WALDBOTT

Carbon monoxide determination in blood. W. YANT and R. R. SAYERS. *U. S.* 1,542,979, June 23. A known quantity of blood is treated with tannic acid and pyrogallol or other reagent capable of destroying the red color of oxyhemoglobin, while leaving the red color of CO hemoglobin, and the resulting color is compared with a standard colorimetric scale prepd. in colors corresponding to definite quantities of CO-hemoglobin in the same quantity of blood.

## C—BACTERIOLOGY

A. K. BALLS

Hemolysins of fungi. VITTORIO PETTINARI. *Arch. farm. sper.* 39, 162-72(1925).—The *Amanita* hemolysin is not a sp. toxic principle of any particular species but a substance widely distributed among diverse species of both toxic and edible fungi. The amt. present varies with different parts of the fungus and is found in the cuticle, gills and stalk in decreasing order. In general the amt. is so small that Ferri's method of demonstrating hemolysins is for all practical purposes sp. for *Amanita phalloides* and the highly toxic fungi. The test can be made much more delicate by using 5% of defibrinated blood in physiol. NaCl soln. instead of entire blood. The substance is partly volatile and the amt. diminishes when the fungus is dried. When injected or administered orally in the amt. present in fungi no appreciable toxic action is observed, and even in the poisoning of human subjects it plays only a secondary role. In the toxicological classification of fungi the group contg. a labile hemolytic principle in Ferri's sense should be omitted. The only hemolytic toxic principle capable in itself of causing poisoning and known to occur in fungi is helvellic acid. The distillate from *Amanita phalloides* is non-toxic; hence the common belief that the fungus contains a volatile poison is erroneous. A. W. DOX

Voges-Proskauer reaction. C. S. LINTON. *Sci. Proc. Iowa State Coll.* 1924; *J. Am. Water Works Assoc.* 13, 547-9(1925).—Time, and possibly temp., of incubation is shown to have an important effect on the results obtained in this reaction. A period of 36-60 hrs. at 30° in Clark and Lubs medium gave + results whereas periods of 5-10 days in the same medium and under similar conditions gave many—results. Acetyl-methylcarbinol, produced in this reaction, appears to be a more or less transient end product. D. K. FRENCH

The uniformity of the chemical mechanism of fermentative sugar dissimilation processes of microbes. A. J. KLUYVER and H. J. L. DONKER. *Verslag Akad. Wetenschappen Amsterdam* 33, 895-914(1924); cf. *C. A.* 5, 1789; 6, 1625; 7, 104, 808; 10, 14, 1305; 15, 1147, 3122; 17, 775; 18, 2181, 2538.—The metabolism of bacteria is the fundamental property on which a classification in natural groups should be based. Similar metabolism indicates similarity of protoplasm, the most characteristic constituent of the bacterial cell. K. classifies sugar-fermenting bacteria into 8 groups according to the main products of metabolism. A new fermentation scheme is given based mainly on the const. intermediate formation of AcOH and on Wieland's dehydrogenation theory of oxidation. The bacterial protoplasm plays the role of the H-transporting catalyst. Its affinity for H varies with the bacterium. The first intermediate product of fermentation,  $C_2H_5O_2$ , is hypothetic; its nature is not discussed. It is converted into lactic acid or into  $HCO_2H$  and AcH.  $HCO_2H$  is dehydrogenated by protoplasm to  $CO_2$ . AcH in presence of water is converted by protoplasm to AcOH. AcH also undergoes condensation to acetylmethylcarbinol and to butyric acid. AcOH is first condensed, then split to  $CO_2$  and acetone. A regeneration of protoplasm follows, whereby the less stable protoplasm- $H_2$  complex evolves  $H_2$ , the more stable yields the H to acceptors. The acceptor is either the substrate, or the intermediate products or foreign substances introduced into the fermentation fluid (phytochemical oxidation of Neuberg). Both reactions can take place simultaneously. The ultimate products may differ according to the conditions of culture or secondary processes. A great number of reactions published by various authors are discussed as evidence in support of the fermentation scheme. The agreement with expl. facts is satisfactory in view of the great difficulties opposing themselves to the detn. of certain products. The theory

permits prediction of the quantity of any fermentation product from the quantity of the other products, the effect of any quant modification of the normal products and the influence of exptl intervention. The dehydrogenation theory accounts for the facts much better than Neuhberg's theory of Camuzzaro rearrangements. The latter cannot explain the formation of isopropyl alc., 2,3-butyleneglycol, mannitol, etc., the formation of AcOH from AcH without the simultaneous appearance of equiv. quantities of mono- or polyhydric alcs., the relation between normal differences in fermentation and the different reducing power of the fermenting fluids toward foreign acceptors, such as molybdic and vanadic acids,  $\text{PhNO}_2$ , methylene blue, S, etc. The new theory also opens a way to the explanation of the relation between dissimilation and assimilation. The occurrence of glycerol in all end products of fermentation becomes intelligible as the reduction equiv. of all surplus oxidations (ketones to acids). When divided into 8 groups from this point of view the sugar-fermenting bacteria present only a few sub groups. Differences in the end products within one group are not essential, since the suppression of one of the early intermediate stages will naturally change the entire course of fermentation. It must however be borne in mind that similar metabolism does not necessarily mean close relationship. Such analogies are occasionally developed in more or less independent phylogenetic series.

MARY JACOBSEN

The catalytic transportation of hydrogen as the fundamental chemical reaction of dissimilation processes. A. J. KLUYVER AND H. J. L. DONKER. *Verslag Akad. Wetenschappen Amsterdam* 34, 237-51(1925); cf. preceding abstract.—The difference between anaerobic and aerobic dissimilation is only in degree not in kind. The catalytic transportation of H is the fundamental reaction of both. The theory of dehydrogenation by protoplasm, developed in the previous paper and enlarged by certain additions, is applicable to any dissimilation process in lower or higher organisms. Mol. O seems to be the only H acceptor which, in accordance with Warburg's theory, requires activation by Fe. In order to withdraw H from other compds. protoplasm must "dislocate" it either directly, by binding part of its affinity or indirectly, by partly satg. the affinity of an O in the mol. An unsatd. condition is thus created and the tendency to intramolecular satn. at the expense of H bonds. H and O affinities of the protoplasm are equally capable of dislocating H but only one of these factors enters into action at a time. Protoplasm with high H affinity has, in analogy to metals, a low O affinity and vice versa. The H acceptor is activated by the same mechanism. The best evidence of the common mechanism of aerobic and anaerobic dissimilations is the gradual passing from one into the other. Many aerobic and anaerobic dissimilations of bacteria, higher plants and muscle tissue are discussed in the light of the theory. The new conception does away with the necessity of creating a new enzyme for each type of reaction. The H affinity of protoplasm is not const. for the same organism, but varies proportionately to the  $p_{\text{H}}$  within the tolerated  $p_{\text{H}}$  range. The conclusion seems to be justified that the dissimilation of any cell is detd. by the H affinity of its protoplasm and the tolerated  $p_{\text{H}}$ .

MARY JACOBSEN

The splitting up of fats by oxidation caused by molds. H. G. DEX. *Verslag Akad. Wetenschappen Amsterdam* 33, 545-58(1925).—Considerable analogy exists between the fermentation and oxidation processes of microorganisms, the higher plant life, and animals. The formation of Me ketones by the splitting up of fatty acids caused by molds proves that the oxidation takes place at the  $\beta$  place of the C atom. The fatty acids, up to and including myristic acid, are adsorbed by the mold mycelium, and thereby hinder the respiratory functions more or less. For this reason the oxidation of these fatty acids stops at the corresponding  $\beta'$  keto acid, which then (perhaps under the influence of a carboxylase) splits into  $\text{CO}_2$  and a Me ketone. It follows also, that the formation of ketones only occurs under unfavorable conditions. They are not normal intermediate products of the oxidative splitting of fats. This ketone formation can occur with nearly all molds, *Oospora lactis* being an exception; this is probably due to the fact that it has extremely powerful oxidizing properties. A large no. of references are given. Also in *Proc. Acad. Sci. Amsterdam* 29, 96-107(1925). J. C. JURAJENS

The antiseptic power of some mercury compounds. G. JOACHIMOGLU AND N. KLISUNIS. *Biochem. Z.* 153, 136-43(1924).— $\text{HgBr}_2$  and  $\text{Hg}(\text{CN})_2$  act best as antiseptics in solns. of  $p_{\text{H}} < 7.8$  or  $p_{\text{H}} > 9.3$ .  $\text{NaHSO}_4$  increases the antiseptic power of the Hg salts, while the addn. of  $\text{NaBr}$  or  $\text{KCN}$  decreases it.  $\text{HgBr}_2$  in  $\text{C}_6\text{H}_6$  or  $\text{Et}_2\text{O}$  is not antiseptic but in  $\text{C}_6\text{H}_5\text{NO}_2$  and glycerol, two solvents with higher dielec. consts., it is antiseptic. In  $\text{CHCl}_3$  with a low dielec. const., however, the action of the  $\text{HgBr}_2$  is not inhibited.

W. D. LANGLEY

The antiseptic influence of sublimate in solvents of different dielectric constants. W. HELLENBRAND AND G. JOACHIMOGLU. *Biochem. Z.* 153, 131-5(1924).—Anthrax spores

were cultured in solns. of  $C_6H_6$ ,  $Et_2O$ ,  $CHCl_3$ ,  $C_6H_5NO_2$ , glycerol, and then in these solvents satd. with  $HgCl_2$ . With pure  $C_6H_5NO_2$  and glycerol the growth was greater than when  $HgCl_2$  was present but in the other cases, no difference was noted. Sublimite in solvents of low dielec. const. has no antiseptic power, while in solvents of high dielec. const. it does possess this power. W. D. LANGLEY

The influence of bacteria upon bile acids. H. LICHT. *Biochem. Z.* 153, 150-64 (1924).—To det. the extent of splitting of bile acids into glycocholic, taurine, and cholic acid, the free amino N and the amino N present after hydrolysis of the bile acids with alkali were measured. After 14 days, in the presence of each of 8 pure cultures, and of fecal bacteria in a  $H_2O$  suspension, practically no hydrolysis was noted. But some change had occurred since the amt. of bile acids, as detd. gravimetrically, decreased. It is probable that this altered bile acid is resorbed from the intestine and transformed again in the liver to the original bile acid, or else further decomposed. W. D. L.

The phosphorus metabolism of some fungi, with especial consideration of *Aspergillus niger*. R. SCHNÖCKER. *Biochem. Z.* 153, 372-423 (1924).—Portions of a sterile phosphate mixt. of known compn. were inoculated with spores of *Aspergillus niger*, *Penicillium W. II*, *Oidium lactis*, and *Dermatium pullulans*, which, after they had been cultured for definite intervals were removed, dried, and analyzed for P, N, sugar, and total acids in the medium. The absorption of P is independent of its concn in the liquid used, but is greater in the earlier stages of growth than in the later. The P which is absorbed does not go directly to aid in spore formation, but is first utilized in the cells. The N and P vary in the same manner, but their proportion is not const. W. D. L.

The problem of acid formation by *Aspergillus niger*. K. BERNHAUER. *Biochem. Z.* 153, 517-21 (1924).—Gluconic acid was isolated from a glucose soln. after it had been acted upon by *Aspergillus niger*. The phenylhydrazide was prepd. and compared with the product obtained by synthesis from glucose. The gluconic acid was not a side product in the formation of citric acid. One group of *Aspergillus niger* gave gluconic or oxalic acid, while another gave citric acid almost exclusively. W. D. LANGLEY

Surface tension of culture media. M. S. MARSHALL. *J. Infectious Diseases* 35, 526-36 (1924).—The effect of each of the ordinary constituents of standard media on the surface tension of distd. water was detd. by a static (immersed ring) method. Considerable reduction was caused by small quantities of beef ext., ascitic fluid, castor-oil soaps, infusion broth, and peptone. With peptone a min. is reached at low concns. A dynamic (falling drop) method gave different abs. values, which, however, are comparative. Detns. of complete media are also made. Bacterial growth did not change the surface tension of infusion broth or of a synthetic medium used, but changes in initial surface tension, made by adding castor-oil soaps, were followed by differences in growth rates and gas metabolism. Correlation reveals no systematic variation. JULIAN H. LEWIS

Studies in yeast metabolism. I. A. K. BALLS AND J. B. BROWN. *J. Biol. Chem.* 62, 789-821 (1925).—Cultures of *Saccharomyces cerevisiae* were grown in a medium of beet sugar molasses and  $NH_4$  salts. Inversion of sucrose begins immediately accompanied by a loss of total sugar from the medium, a corresponding loss of total solid matter, and an appearance of  $CO_2$  and  $EtOH$ , these changes taking place most rapidly during the early hrs. of the expt. After 8 hrs the disappearance of sugar and total fermentable solids is practically complete and the alc. concn. and H-ion concn. of the liquid are at their max. Alc. disappears gradually thereafter, partly due to the aeration maintained during the expts., and partly by conversion to some other compd. This gradual loss of alc. is accompanied by the slow but steady production of  $CO_2$  without further sugar loss to account for it. A marked increase in the wt. of the yeast occurs and the log. law of yeast multiplication holds when this wt. is measured instead of cell count. The wt. continues to increase for a long time after all the sugar has disappeared and proceeds logarithmically with a velocity const. roughly  $1/10$  that of the prior log. phase. Addn. of more sugar after the 1st supply is exhausted produces further yeast growth with all the usually attendant changes. The sugar is not necessary to yeast growth but greatly increases its speed. The spent liquor of the mash is not appreciably toxic to new yeast growths. A small quantity of unassimilable reducing substance is formed during the disappearance of sugars. Changes in N concn. in general parallel the wt. increase throughout the entire time of the expt., indicating that N is used merely as the yeast grows. Carbohydrates exert no N-sparing effect. The N is not taken from the air but comes both from the molasses and the  $NH_4$  salts present; both forms are used in fairly definite proportion which remains reasonably const. independent of variations in the amt. of either. II. Carbon dioxide and alcohol. J. B. BROWN AND A. K. BALLS. *Ibid* 823-36.—The production of alc. by the aerated yeast culture is

much less than that required by the usual fermentation equation and the amt. decreases gradually after the sugar is all decompd. until finally the liquid contains none. On the other hand, the amt. of  $\text{CO}_2$  liberated is greater than would be predicted on the basis of sugar removal and its production continues after the sugar is entirely gone. In similar expts. using alc. solns and yeast, the alc. likewise disappears,  $\text{CO}_2$  is formed and the yeast gains slightly in wt. These changes do not occur under anaerobic conditions. The opinion is advanced that the removal of alc. is an oxidation process which does not involve metabolism of the C by the yeast cells, that products other than  $\text{CO}_2$  are formed by this means, and that the increase in yeast wt. is due to a development of the cells rather than to their multiplication. A. P. LOYTHROP

The distribution of nitrogen in the protein fraction of tubercle bacilli after removal of tuberculinic acid. T. B. JOHNSON AND R. D. COGHILL. *J. Biol. Chem.* 63, 225-31 (1925).—Detns. of the N distribution in the protein of tubercle bacilli by the Van Slyke method show the presence of a high % of hexone bases (28.62, 29.71 and 33.68) and only a trace of cystine. There is a very close relationship between these figures and those obtained by Chibnall on cell proteins sepd. from the cytoplasm of the leaves of spinach, alfalfa and ensilage corn. The results confirm those obtained by Johnson and Brown (*C. A.* 17, 1261). A. P. LOYTHROP

The influence of the paratyphoid group on the fermentation of lactose by *B. coli*. H. MIZUHARA. *Centr. Bakt. Parasitenk. I Abt., Orig.* 92, 20-7 (1924).—The presence of the paratyphoid group lessens gas formation from lactose by *B. coli*. Complete inhibition was noted once. JOHN T. MYERS

The importance of the reaction of gonococcus cultura medis. TORAHIKO IKOWA. *Centr. Bakt. Parasitenk. I Abt., Orig.* 92, 61-4 (1924).—Every gonococcus strain which grew scantily on alk. ascites agar, and failed to grow on horse serum agar, grew well after the addn. of an org. acid; 0.4% N citric acid was best. JOHN T. MYERS

The technic of anaerobic cultures. III. Glass fruit jars as desiccators for culturing anaerobes. BRECKENFELD. *Centr. Bakt. Parasitenk. I Abt., Orig.* 92, 129-30 (1924). JOHN T. MYERS

The differentiation of bacteria of the colon-typhoid group by staining reactions. J. KABELIK AND WALTER ROSENZWEIG. *Centr. Bakt. Parasitenk. I Abt., Orig.* 92, 197-201 (1924).—No practicable methods were found but possibilities were suggested. JOHN T. MYERS

Dimethyl-p-phenylenediamine in mediums for anaerobes, and the behavior of several serobes on this medium. I. NIKOLAUS KOVACS. *Centr. Bakt. Parasitenk. I Abt., Orig.* 92, 315-20 (1924).—Agar contg. 0.05% of dimethyl-p-phenylenediamine gave the same cultural results with anaerobes as did dextrose agar, without the disadvantages of the latter. It can also be used for differentiating streptococci from staphylococci, because it inhibits the latter. It inhibits *B. dysenteriae* Shiga but not *B. dysenteriae* Flexner. JOHN T. MYERS

The volatility and constancy of heat resistance of the d'Herelle bacteriophage. GERTRUD MEISSNER. *Centr. Bakt. Parasitenk. I Abt., Orig.* 92, 324-7 (1924).—The lysis was neither volatile nor heat resistant. JOHN T. MYERS

Comparative studies on the products of *B. coli* and *B. typhosus* with special reference to Endo medium. J. BARNEWITZ AND H. FLECKE. *Centr. Bakt. Parasitenk. I Abt., Orig.* 92, 359-62 (1924).—HCl will not restore the color to basic fuchsin which has been decolorized with  $\text{Na}_2\text{SO}_4$ , but lactic acid does at 37°. JOHN T. MYERS

Nitrate-forming bacteria. J. SACK. *Centr. Bakt. Parasitenk. II Abt.,* 92, 15-24 (1924).—See *C. A.* 19, 999. JOHN T. MYERS

Further indirect evidence that anaerobes tend to produce peroxide in the presence of oxygen. J. W. M'LEOD AND J. GORDON. *J. Path. Bact.* 28, 147-53 (1925).—Although catalase is not able to promote the growth of anaerobes in direct contact with air, it can raise the level of growth in a deep agar tube almost to the surface. In the presence of a high concn. of catalase in the form of fresh blood the appearance of a green ring in chocolate agar cultures of anaerobes is much delayed and decreased. The same thing occurs in cultures of peroxide-forming bacteria like the pneumococcus. The presence of a thermostable, nonperoxide-reacting substance (presumably glutathione) is not essential for the formation of a green ring by anaerobes but appears to promote it as well as favor growth. There is evidence that  $\text{H}_2\text{O}_2$  is formed in anaerobic cultures. The presence of catalase does not check the penetration of O into a solid medium. JOHN T. MYERS

The relations between the reducing powers of bacteria and their capacity for forming peroxide. J. W. M'LEOD AND J. GORDON. *J. Path. Bact.* 28, 155-64 (1925).—A necessary consequence of bringing a reducing mechanism into contact with O is the

formation of  $H_2O_2$ . Such a mechanism is the production of nascent H. All bacteria do this but the activity of different species varies. All bacteria which have such a mechanism and are free from catalase produce  $H_2O_2$ . There is a parallelism between the reduction of glutathione, the soln. of cystine, and the production of  $H_2O_2$  by bacteria, provided the influence of catalase and the sensitiveness to  $H_2O_2$  are considered.

JOHN T MYERS

The investigation of phytopathogenic bacteria by serological and biochemical methods. RALPH ST JOHN BROOKS, K. NAIN AND MABEL RHODES. *J. Path. Bact.* 28, 203-9 (1925).—Bacteria associated with diseases of plants were examd by cultural, serological, and biochem. means. Appearance on agar divided them into 3 groups: fluorescent, yellow and white. Biochem. reactions within the first 2 groups were fairly const. Serological methods revealed important groupings which are still under investigation.

JOHN T MYERS

Time of combination of diphtheria toxin with living tissues. A. T. GLENNY AND BARBARA E. HOPKINS. *J. Path. Bact.* 28, 261-72 (1925).

JOHN T MYERS

Studies in group agglutination. II. The absorption of agglutinin in the diphasic salmonella. F. W. ANDREWS. *J. Path. Bact.* 28, 345-9 (1925).—A method is described by which the relative proportions of 2 agglutinogens in a bacterium can be quant. detd.

JOHN T MYERS

The resistance to phenol of *Staphylococcus aureus*. GEO. F. REDBISH. *Am. J. Public Health* 15, 534-8 (1925).—Considering the known specificity of disinfectant action, it seems highly desirable to test disinfectants with those organisms against which each is to be used, or, if for general disinfection, against a variety of pathogens representing the most important groups. *Staphylococcus aureus* is the most common cause of suppuration and was selected for study as the representative of the pyogenic group. Twenty-five strains, 22 of which were recently isolated, were tested as to their resistance to phenol. A fresh, resistant strain of this organism will resist 1-70 diln. of phenol for 10 min., and 1-80 diln. for 15 min., and usually resist 1-60 diln. for 5 min. Therefore, any strain of *Staphylococcus aureus* to be used for testing disinfectants must not show a lower resistance to phenol than indicated here. It is suggested that similar standards be detd. for other species representing various groups of pathogens.

G. F. REDBISH

Contribution to the chemistry of decomposition of proteins and amino acids by various groups of microorganisms. S. A. WAKSMAN AND S. LOMANITZ. *J. Agr. Research* 30, 263-81 (1925).—A study of the nature of decompn. of certain pure amino acids and casein by 2 fungi, 2 bacteria and one *Actinomyces* showed that not all organisms attack proteins and amino acids alike. The 2 fungi utilized the various amino acids in the proteins both as sources of C and N, but the amt. of growth and  $NH_3$  accumulation depended in the absence of carbohydrates upon the available C in the amino acid mol.  $NH_3$  can therefore not be used as an index of the proteolytic activities of organisms when the C content of the medium is not considered. The 2 bacteria tested behaved differently in that one rapidly hydrolyzed proteins but was unable to attack simple amino acids while the reverse was true of the other, and both combined in a casein media decompd. it more rapidly to  $NH_3$  than either alone. The *Actinomyces* was found to be capable of utilizing amino acids and proteins as sources of energy, thus allowing an accumulation of  $NH_3$ , even in the presence of dextrose. It is concluded that  $NH_3$  formation by microorganisms from amino acids depends upon the C:N ratio of the compd. as well as upon the nature of the organism as influenced by its utilization of energy.

W. H. ROSS

Acetic bacillus of Japan. K. MIYAJI. *J. Sci. Agr. Soc. (Japan)* No. 263, 1-7 (1924).—Thirty varieties of acetic acid bacteria were isolated from vinegar factories in Japan. Morphologically and physiologically they fall into 3 large groups. The various strains were not equally adapted to the production of a high grade of acid. Certain amino acids were vigorously attacked by these bacteria. The usual decompn. products were isolated.

F. W. TANNER

Production of hydrogen sulfide by members of the colon group of bacteria. MUL-SOW AND PAINE. *Proc. Iowa Acad. Sci.* 1924; *Abstracts Bact.* 8, 295.—Pb acetate agar is prepd. by adding the Pb acetate soln. before tubing and sterilizing the medium. There are only a few strains of *B. coli* which give  $H_2S$  from peptone, and only a very few strains fail to give the gas from cystine or  $Na_2SO_4$ .

F. W. TANNER

Theory of dye utilization in bacteriological media. C. H. WEREMAN. *Sci. Proc. Iowa State College* 1924; *Abstracts Bact.* 8, 293-6.—Various phenomena influencing the use of dyes in bacteriol. media are discussed, mostly with reference to eosin and methylene blue. Reactions similar to those on eosin methylene blue agar are obtained

in broth,  $\epsilon$ , green scaly ppt. on the surface and dark ppt. at the bottom of *B. coli* cultures. *B. aerogenes* reduces the dye more readily than *B. coli*, especially if the temp. is below 37°. Bacteria pptn. is enhanced by the amphoteric behavior of organisms and reduction of the  $\text{pH}$  to near their isoelec. point, particularly in the case of *B. coli*. Increasing the lactose up to 2% prolongs the permanence of the green sheen on *B. coli* colonies. Other dye combinations offer differentiations of *B. coli*, *B. aerogenes* and other members of the colontypoid group. Azure II, thionine, safranin and crystal violet with eosin gave good results when used in proportions similar to those employed in eosin-methylene blue. Congo red may be used in place of eosin. F. W. TANNER

JORGENSEN, ALFRED: Micro-organisms and Fermentation. 5th ed. Thoroughly revised. Philadelphia: J. B. Lippincott. \$12.00

## D—BOTANY

B. M. DUGGAR

Water content, a factor in photosynthesis. R. H. DASTUR. *Ann. Botany* 38, 779-88(1924).—As the leaf becomes older, cessation of photosynthetic activity, indicated by the disappearance of starch, first appears at the margins and apices and thence spreads inward between the smallest veins. Photosynthetic activity persists longest in narrow zones bordering the larger vascular bundles, but ceases long before the fall of the leaf. The disappearance of starch is preceded by disintegration of the chloroplasts of the cells concerned. That the cessation of photosynthesis is due to a decrease in water supply was indicated by placing the petioles of leaves in eosin, which rose freely into the vessels of normal areas but entered only as traces into those starch-free areas. No changes in structure which would account for loss of function in these vessels could be made out. Decline in photosynthetic activity at leaf margins and apices is due to the fact that the water-supplying capacity of the vessels is a const. which does not increase in leaf area and transpirational loss. The consequent shortage falls most heavily on the cells most distant from the veins. Willstätter and Stoll failed to get const. values on the assimilation of  $\text{CO}_2$  by leaves of the same species because it is difficult to select leaves which are in the same stage of photosynthetic activity. JOSEPH S. CALDWELL

The growth of the cotton plant in India. I. The relative growth rates during successive periods of growth and the relation between growth rate and respiratory index throughout the life cycle. R. S. INAMDAR, S. B. SINGH AND T. D. PANDE. *Ann. Botany* 39, 281-311(1925).—Three series of cotton plants, planted May 14, June 6 and July 15 in pots, were compared as to fresh weight, dry weight, leaf area, ratio of leaf weight to leaf area and respiratory index of leaves, shoot and root. Detns. were made weekly throughout the period of growth. Atm. conditions during the period are described in general terms, no detailed data as to temps. and humidity being given. Flowering in the first series began on the 83rd day, in the second on the 64th day, in the third on the 47th day. The relative growth rate increases to a max. which was attained in the 8th week in the first series, but which shifts backward as the vegetative period shortens, occurring in the 3rd week in the 3rd series. The growth rate shows no agreement with leaf weight and leaf area in young plants which have not attained full assimilative capacity, or in plants near the end of the period of active growth, but is in fair agreement for an intermediate period. There is no very close agreement between growth rate and rate of respiration of the tissues. The respiratory rate is an index of the sum total of photoplasmic activities, but apparently has no influence in detg. increase or decrease in growth rate. Companion cultures of *Impatiens* gave results in broad general agreement with those for cotton. JOSEPH S. CALDWELL

Polarity phenomena in sea-kale roots. W. NELSON JONES. *Ann. Botany* 39, 359-72(1925).—Root cuttings of sea-kale (*Crambe maritima*) show well-marked polarity in regenerating roots and shoots which is little affected by gravity. Buds can be induced to form at the root ends of cuttings by centrifugal force, or by warming the area ( $2^\circ$  is sufficient) but root formation cannot be so shifted. In very short lengths of root, shoots appear at both ends, roots at one only. Treatment with elec. currents, acids or alkalis does not affect polarity. There is no const. difference in elec. potential or resistance between the 2 ends. With the exception of the effects of gravity and of centrifugal force, the results agree with Child's conception of metabolic gradients. J. S. C.

Studies in the genus *Fusarium*. II. An analysis of factors which determine the growth forms of certain strains. W. BROWN. *Ann. Botany* 39, 373-403(1925).—Certain strains of *Fusarium* originally isolated from decaying apples have been studied with respect to the influence of nature and concn. of nutrient medium upon growth

form. Increase of phosphate as neutral salt decreases aerial mycelium formation and increases sporulation. Increase of acid phosphate has the opposite effect. Increase of dextrose increases aerial mycelium; increase of starch increases sporulation. Increase of N (as asparagine,  $\text{KNO}_3$ , peptone or  $\text{NH}_4\text{Cl}$ ) increases the staling effect. Pigment production is favored by a low concn. of N or by a high ratio of carbohydrate to N.

JOSEPH S. CALDWELL

The regional and seasonal distribution of potassium in plant tissues. E. S. DOWNING. *Ann. Botany* 39, 459-74 (1925).—Material frozen by solid  $\text{CO}_2$  was sectioned while frozen, K being demonstrated by the hexamtrite reagent of the Macallum Co. K is absent from the wood but abundant in meristematic tissues of 5 general roots of *Picea canadensis* during the winter. It was abundant in the tracheides and phloem of rootlets. Stem tips, root tips and apical buds are poor in K when dormant but rich in it when active. In leaves, the tracheides are K-free, while phloem and medullary rays are rich in it, the largest amts. being present in the bordered pits leading from the rays to the tracheides. In chlorophyllose cells, K is localized in the vicinity of the laked chloroplasts during the winter, in summer it is rather evenly distributed through the cell as granular reticulations about the chloroplasts, probably adherent to them. In Marquis wheat K is localized in the embryo and the aleurone layer, the endosperm being nearly free. After 15 days germination the aleurone layer is K-free, and the K in the embryo is mainly localized in the scutellum and stem and root apices. In employing Macallum's method, care must be exercised to avoid error due to the fact that  $\text{NH}_3$  reacts with the reagent in the same way as K.

JOSEPH S. CALDWELL

The coagulation of pectin. W. KOPACZEWSKI. *Bull. soc. chim. biol.* 7, 419-28 (1925).—The action of Ca salts is not sp., they can be replaced by Ba, Sr, or Mg salts, and the action of Cu or Fe salts is much greater. The coagulating action of these salts in the presence of pectase is much greater than that of pectase alone. The presence of alk. salts is necessary for the transformation of pectin by the enzyme though they take no part in the formation of the coagulum, the same concn. of Ca being necessary to produce coagulation, in the presence or in the absence of alk. salts, once the action of the pectase is accomplished. The optimum reaction for pectase is neutrality. Its action produces an acid reaction in the presence of electrolytes after which it is not coagulated by alc. No purely chem. theory will explain pectin coagulation.

A. T. CAMERON

Catalase activity in dormant apple twigs: Its relation to the condition of the tissue, respiration and other factors. A. J. HEINICKE. *Cornell Agr. Expt. Sta., Mem.* 74, 33 pp (1923); cf. *C. A.* 18, 1007, 1687.—The data obtained on the bark of dormant twigs agree in general with similar data on apple leaves (*C. A.* 18, 1007). The ability of such tissue preps. to hasten the decompn. of  $\text{H}_2\text{O}_2$  is unquestionably influenced by the condition of the tissue at the time of sampling, and may therefore serve, along with other measures, as a convenient and sensitive indicator of physiol. responses of fruit trees to various cultural conditions or treatments. No attempt is made to explain the nature or function of catalase in tissue, but it is not unreasonable to assume that, occurring as it does, in all active tissue, it probably has some vital role in metabolism. The rate of catalase and rate of  $\text{CO}_2$  production do not necessarily tend in the same direction; the 2 processes are probably not closely correlated. In general a basis is afforded for suggesting that the presence of growth-producing substances favors catalase activity, while those substances tending to inhibit vegetative activity have a retarding influence. Among the former org. nitrogenous materials are probably the most influential, while the presence of carbohydrates is the chief cause of the depression in catalase activity.

P. R. DAWSON

The relative importance of the carbon dioxide of the soil and of the atmosphere in plant growth. E. H. REINAU. *Technik in der Landwirtschaft* 5, 95-103 (1924); *Intern. Rev. Sci. Practice Agr.* 2, 864-7 (1924).—The exptl. data and calcs. presented lead to the conclusion that while air and soil both play their part in supplying  $\text{CO}_2$  to the leaves, the soil is the chief source, supplying on an av. about 10 times the amt. yielded by the air. It was shown that the soil is able to supply all the  $\text{CO}_2$  required by plants. Justification is shown for the interest in all investigations directed at the detn. of how far  $\text{CO}_2$  production by the soil is affected by methods of cultivation, fertilizers and the nature of the soil.

P. R. DAWSON

Changes in the percentage of vitamin A and in the nature of albumin during the germination of katjang-idjoe (*Phaseolus radiatus* L.). W. F. DONATH. *Repts. Dutch Indian Med. Civil Service* 4, 344-62 (1924).—Expts. on rats to det. the relative content in vitamin A of katjang-idjoe and its sprouts (tao-geh). Vitamin A is synthesized in the sprouts of katjang-idjoe during the first 8 days of germination and increases with the age of the sprouts. The greater portion of the vitamin is present in the leaves and

sprouts while very little is found in the roots. The ability of the albumin of the katjang idjoe to compensate for the deficiency in the amino acids of rice albumin, which is absent in the unsprouted bean, develops on germination. H. J. DEUEL, JR.

Something theoretical and practical about calcium oxalate. FRITZ NETOLITZKY. *Chem. Ztg.* 49, 397(1925).—In books on botany N. found the statement that the  $\text{CaC}_2\text{O}_4$  in plants contains for those belonging to the monoclinic system 2 mols. of crystal water, and for those of the tetragonal system 6. As the artificial crystals only exist in the mono- and trihydrate forms, N. examd. the crystals he obtained from several plants, and found that they contained the normal mol. of crystal water. He concludes that the error lies in using the old formula. The article closes with a discussion of a possible practical extn. of some plants and barks which are often exceedingly rich in  $\text{CaC}_2\text{O}_4$  crystals, instead of using the processes used at present. J. C. JURJEVS

The bio-genesis of Mahua oil. G. J. FOWLER AND TALWAR DINANATH. *J. Indian Inst. Sci.* 7, 273-84(1924).—Microchemical, macrochemical and enzyme studies of the fruit were made at weekly intervals throughout their development. Diagrams are given showing the changes occurring in sugar, tannin, chloroform extract, proteins and starch in the husks, of starch, tannins, alcohol extract and chloroform extract in the seed and of the I value, acid value and refractive index of the oil. No starch was found in the seeds at any stage. The  $\text{CHCl}_3$  extract rises as the alcohol extract, tannins and starch decrease. The authors therefore conclude that oil is formed at the expense of carbohydrates and possibly tannins. Free fatty acids are at a maximum early and then decrease rapidly. H. R. KRAVILL

Normal development of corn utilizing only nitrogen fixed by bacteria. GEORGES TRUFFAUT AND BEZSSONOV. *Compt. rend. soc. biol.* 91, 1077-8(1924).—In the presence of N-fixing bacteria corn develops normally and reaches maturity in mediums devoid of org. nitrogenous matter. The secretions of the corn rootlets suffice to furnish the bacteria with the required energy. S. MOROULIS

Selective absorption of chlorine ions; and the absorption of water by the leaves of the genus *Atriplex*. J. G. WOOD. *Australian J. Exptl. Biol. Med. Sci.* 2, 45-56(1925).—Leaves were placed in jars furnished with a water seal and an atomizing app. which could be worked from the outside to keep the humidity const. The tests were conducted in the dark to eliminate the effects of photosynthesis, and at a temp. of 35° and a relative humidity of 85%. Under these conditions the wt. of water absorbed by the leaves was detd. for 22-hr. periods. In the 9 species of *Atriplex* studied the figures ranged from 0.7 to 1.135 g. per g. of dry matter in the leaves. Analysis of the sol. ash of *A. nummularium* gave Cl 7.78%, K 6.20 and Na 6.0. Although this analysis was made at the close of the wet season when the salt content is at a min., and this species has a lower percentage of salts than any species of *Atriplex* studied except *A. limbatum*, the salt content is abnormally high for plants. Analyses for Cl and NaCl were made of soil in which were grown the 9 species studied. The amt. of salt in the leaves is a function of the amt. of salt in the soil. It shows seasonal variations and beyond a certain max. the plants are killed. The accumulation of salt in the leaves occurs principally in the vesicles. *Atriplex* species are the only plants which exhibit a high selective absorption of chlorides, i. e., 12 to 30%. In other tomentose plants the chloride content is less than 7%, and in plants with cutinized leaves less than 2%. Osmotic pressure in the leaves of *A. tataricum* and *A. paludorum* was estd. at 40 and 65 atm., resp. The greatest concn. of salt occurs in the veins of the leaf and in the cubical chlorenchyma surrounding the veins. Very little occurs in the thin-walled assimilating cells. The mechanism of water absorption in *Atriplex* species is not accounted for by osmotic pressure alone. The root system of *Atriplex* is poorly developed and apparently the success of these plants is due to their ability to absorb water through the leaves. L. W. RIGGS

Kakishibu. II. S. KOMATSU, N. MATSUNAMI AND M. ISHIDA. *Mem. Coll. Sci. Kyoto Imp. Univ.* 8A, 43-9(1925); cf. C. A. 18, 820.—The volatile acids of shibu are butyric with a much smaller quantity of acetic. These acids appear to be formed at the expense of the carbohydrates *d*-glucose and *d*-fructose. Mannitol was found in the fermented kakishibu but not in the fresh or in the kaki-fruit. The mucilage fraction of the shibu on exposure to the air forms a jelly-like film which gradually increases in thickness. It appears to be a mixt. of mucilage and pectin. Shibuo is also present. L. W. RIGGS

Selective absorption of potassium by plants. G. ANDRÉ AND E. DEMOISSY. *Compt. rend.* 180, 1052-4(1925).—K and Na were detd. in the exterior, middle and interior zones of sections of cattle beets on July 31 and Oct. 31, resp. The ratios K/Na for the zones mentioned on July 31 were 63, 72 and 100, resp. On Oct. 31 the corre-

sponding figures were 96, 99 and 100. The action is attributed to the superlative selective absorptive power of K, as compared to that of other metals. L. W. RIGGS

Linear relation between the successive quantities of phosphoric acid and nitrogen in the leaves of the well nourished grapevine. H. LAGATU AND L. MAUME. *Compt. rend.* 180, 1179-81 (1925); cf. C. A. 19, 696, 842.—Detos. of  $P_2O_5$  and N were made about the middle of each month from May to Oct inclusive. The  $P_2O_5$  figures were 0.736, 0.576, 0.544, 0.512, 0.320 and 0.400, resp. The corresponding figures for N were 4.50, 3.14, 3.04, 2.78, 1.62 and 2.17, resp. It was found that if the value for  $P_2O_5$  were multiplied by 6.339 and 0.409 subtracted from the product, the result expressed very nearly the analytical values for N. This relation may be of value in detg. the food requirements of the plant. L. W. RIGGS

Segregation of carbohydrates in maize pollen. A. E. LONGLEY. *Science* 61, 542-3 (1925).—Additional evidence from a study of properly stained maize pollen of 200 plants grown from the horny seeds of an  $F_2$  hybrid of waxy horny showed that these pollen grains may be sepd into 2 distinct classes. The stage at which the 2 classes are most sharply sepd, is just before anthesis, but the distinction exists at all times when there are granules of carbohydrates stored in the pollen grain. L. W. RIGGS

Presence of trehalose in yeast. ELIZABETH M. KOCH AND F. C. KOCH. *Science* 61, 570-2 (1925).—Forty lbs. of compressed yeast were air dried and were subjected to continuous extn., first with  $Et_2O$  for 18 hrs., followed by 4 portions of 90 to 95% alc for periods of 18 to 20 hrs each. These combined alc exts. were stored in large bottles and seeded with crystals obtained in a previous expt. After 8 to 10 days crystals began to form on the sides of the bottles. When growth of the crystals appeared to cease, the alc. was decanted and the crystals were dissolved in hot glacial  $AcOH$ , the soln was cooled and 10 to 12 vols. of acetone were added. The creamy ppt was filtered out and was washed several times with acetone. A water soln of this ppt. was decolorized with charcoal, then concd. to a sirup and was dild. slowly with hot alc. to 70 or 80%. Acetone was added until the soln just began to appear milky when it was seeded with crystals and cooled under a bell jar. Large crystals similar to rock candy were formed within 24 hrs. These after 4 or 5 recrystns gave const. near those of trehalose. L. W. RIGGS

Alkaline reaction of dew on cotton plants. C. M. SMITH. *Science* 61, 572-3 (1925); cf. C. A. 18, 545.—Reply to Mulla, cf. C. A. 18, 3408. Cf. Power and Chesnut, C. A. 19, 844. L. W. RIGGS

Titanic acid in the potato tuber. W. P. HEADDEN. *Science* 61, 590 (1925).—If  $TiO_2$  is found in the ash of field-grown plants, it may have originated in the dust and sand blown upon the plant. The ash of well washed tubers contained 0.03% of titanic acid. L. W. RIGGS

Some physical and chemical properties of carotin and the preparation of the pure pigment. F. M. SCHERTZ. *J. Agr. Research* 30, 469-74 (1925).—The soly. of carotin in abs. alc., petroleum ether (b. p.  $30^\circ$  to  $50^\circ$ ) and specially purified  $Et_2O$  amounts to 15.5, 626 and 1,005 mg. per l, resp., at  $25^\circ$ . Solns of carotin in abs. alc. and petroleum ether are extremely stable when kept in an ice box, but  $Et_2O$  solns decompose rapidly under the same conditions. Crystals of carotin may be stored in alc., or petroleum ether, in open containers for some time without oxidation and may be stored permanently in these solvents if sealed in ampules. A yield of 1.13 g. of pure carotin (m. p.  $174^\circ$ ) per bushel was obtained by a method which is described for its prepn. on a small scale from carrots. Some physical and chemical properties of xanthophyll and the preparation of the pure pigment. *Ibid* 575-85.—A detailed description is given of the prepn. and purification of xanthophyll from dried green leaves. Its soly. in petroleum ether (b. p.  $50^\circ$  to  $55^\circ$ ), abs. alc., abs. MeOH and pure anhydrous  $Et_2O$  amounts to 9.5, 201.5, 134.9 and 952 mg. per l, resp., at  $25^\circ$ . When kept in an ice box, xanthophyll is unstable in  $Et_2O$  solns., very stable in abs. alc. and slightly unstable in petroleum ether. In the dry state xanthophyll oxidizes more readily than carotin. In soln. it also oxidizes more readily than carotin when kept in an ice box, but the reverse is true when the solns. are exposed to sunlight at room temp. W. H. ROSS

Physiological studies on cereals. III. The occurrence of polypeptides and amino acids in the ungerminated maize kernel. S. L. JOHNS. *J. Agr. Research* 30, 587-92 (1925); cf. C. A. 18, 2909.—Polypeptides and free amino acids are shown to be present in the ungerminated corn kernel and to be formed in it. The amino N in 3 varieties of ungerminated corn averaged 0.045% calcd. on the basis of the oven-dried kernel, or 2.88% on the basis of the total N. The corresponding values found for the peptide N in the same varieties were 0.052 and 3.22%, resp., and for the acid amide N, 0.024 and 1.50%. W. H. ROSS

The influence of radioactive water on the germination of plants. D. VIDAL. *Compt rend agr France* 11, 402-6(1925)—Germinating grain was stimulated by the use of radioactive Pb salts. Emanations gave contradictory results. F. M. S.

The presence of certain organic compounds in plants and their relation to the growth of other plants. R. C. COLLISON. *J. Am Soc. Agron.* 17, 58-68(1925).—The type of injury which results from straw may be caused by the formation of one or more of the following compds: tyrosine, dihydroxystearic acid, vanillin and coumarin. F. M. S.

Nitrate of soda in the nutrition of the tomato. PAUL WORK. Cornell Agr. Expt Sta., *Memoir* 75, 86 pp (1924).—Graduated single applications of  $\text{NaNO}_3$  up to 32 g. per 14 in. cubical box resulted in increased vegetation and fruit, and applications higher than 32 g. decreased from the max. A small quantity of  $\text{NaNO}_3$  in small doses gave better results than the entire quantity in a single application. Large applications did not give heavy vegetation or fruiting. The hypothesis is set forth that the injurious influence of higher applications of  $\text{NaNO}_3$  is due to its effect as a factor in the environment of the plant, reducing the availability of  $\text{H}_2\text{O}$  supplied rather than through its effect as an internal poison. The max. N content in the leaves of tomato plants was 0.390% green wt. basis and the lowest was 0.173%. The N content of leaves above 0.30% seems to be essential for vigorous vegetation and fruiting. The max. N content of stems was 0.206%. Vigorous and well fruited plants contained above 0.120%. There is no relation between amt. of  $\text{NO}_3$  applied to the soil and the concn. of total carbohydrates in the plants. In N-starved plants N is low and carbohydrates are high. The carbohydrate content of leaves ranged from 0.92% green wt. basis to 5.97% and in stems from 1.42 to 8.21%, the high figures are from N-starved plants. Vigorous vegetative plants showed a range from 0.92 to 3.66% in leaves and 1.42 to 3.30% in stems. There was no indication that high or low carbohydrate content inhibits either vegetative or reproductive activities of the plants. J. J. SKINNER

A study of growth in summer shoots of the apple with special consideration of the role of carbohydrates and nitrogen. E. M. HARVEY. Oregon Agr. Expt Sta., *Bull.* 200, 51 pp (1923).—Moisture, sol. solids, phlorhizin and N which tend to decrease in apple tree shoots through the growing season are most abundant in the shoot tips and least abundant in the base. Insol. solids, sugars, polysaccharides and total carbohydrates, which increase through the growing season, are least abundant in the tip and most abundant in the base. The chem. changes produced in the upper portion of shoots by defoliation are indicated by an increased percentage of water, sol. solids, phlorhizin and N, and by a decrease of insol. solids, sugar, starch, pentosans, total polysaccharides, total carbohydrates and the carbohydrate-N ratio. Ringing caused a decrease in the moisture, sol. solids, phlorhizin and N, in the upper part of the shoot and an increase in the insol. solids, sugar, starch and pentosans. Ringing plus defoliation produced striking chem. changes. Suggestions are made for applying the results to tree pruning. J. J. SKINNER

Stimulation of growth in barley and oats by wetting the seed with a solution of magnesium chloride. H. J. VON FEILITZEN. *Kgl. Landbruks Akad. Handl. Tid.* 64, 68-82(1925).—Sound seeds of oats and barley were treated with a 5% soln. of  $\text{MgCl}_2$  for 4 hrs. For comparison seeds were also treated with Uspulum and tap water. Detn. of the percentage of germination and rate of growth showed that treatment with  $\text{MgCl}_2$  produced no effect. C. O. SWANSON

Detection of some enzymes in extracts of fresh plants prepared by the Golar-Siegfried method. "V." *Schweiz. Apoth. Ztg.* 63, 161-3, 178-80(1925).—Oxidases or peroxidases were found to be distinctly present in fluid and dry exts. of horseradish root in spite of pasteurization at 65-70° and evapn. *in vacuo*; they were present in traces in exts. of *Aesculus*, but absent in exts. of gentian root, wormwood and walnut. Reductases and catalases were absent in all of these. Positive reactions for diastases were obtained only with exts. of horseradish root and *Aesculus*. The method used merits further study. S. WALDBOTT

A statistical study of the composition of potato tubers. J. J. WILLAMAN AND R. M. WEST. *Minnesota Studies in Plant Science* No. 5, 211-27(1924); cf. *C. A.* 18, 2543.—The compn. of American potato tubers is not affected by varietal differences so much as by environmental effects. The most marked varietal difference is that between the early and the late maturing varieties; the early types are low in dry matter, and high in ether ext., minerals and N. The effect of soil can be detected only in a general way in the present data; it appears that, in comparing loam, sand and clay soils, the loam induces the highest dry matter, N, and ether ext., the sand the lowest dry matter, and the clay the lowest N. Tubers grown in the southern part of Minnesota are con-

siderably higher in N than those grown in the northern part. During the growth of the tubers there is a steady increase in dry matter up to the time the vines begin to die, and the ratios among the various constituents remain rather constant. Large and small tubers of the same stage of maturity have the same composition. There is a strong positive correlation between sp. gr. and dry matter, but no correlation of significance between sp. gr. and either N or carbohydrate (dry basis). The N is correlated negatively with carbohydrate and with ash, and positively with ether ext. The ash bears a negative relation to all org. constituents. The available facts concerning the composition and properties of potato tubers warrant the conclusion that it should be possible to breed a variety with a higher proportion of protein to carbohydrate, and still with desirable culinary properties.

J. J. WILLANIAN

Colloid chemistry of the synthesis and degradation of the cellulose framework of the plant, "lignin" and wood fiber. H. WISLICENUS. *Cellulosechem.* 6, 45-58 (1925).—W. gives a résumé of his work on the dependence of lignification on climatic factors, the colloid contents of cambial and spring saps, the comparison of vegetable fibers with fibrous alumina, the changes in properties of cellulose on grinding, etc. He reiterates his theory that lignin is a heterogeneous mixt., consisting of the sum total of all wood-producing substances of high mol. wt. present in the formative or cambial sap that are deposited primarily by adsorption, later by colloidal aggregation ("Admassierung oder Komolierung") on the surface of the cellulose fiber, during the period of summer's growth.

LOUIS E. WISE

## E—NUTRITION

PHILIP B. HAWK

Studies of metabolic exchanges in high mountain and in plain. III. The resistance of the animal organism to fasting in rarified air. A. COSTANTINO. *Arch. ital. biol.* 73, 55-60(1924); cf. *C. A.* 18, 1689, 2544.—During the first 2 days of a fast in rarified air (480-490 mm. Hg pressure) rabbits mobilize and oxidize carbohydrate, sparing especially protein.

A. T. CAMERON

Osteomalacia in China. J. P. MAXWELL AND L. M. MILES. *Proc. Roy. Soc. Med.* 18, Sect. Obstetrics Gynecol., 48-66(1925); cf. *C. A.* 19, 850.—A toxic process may arise through unbalanced protein consumption (cereal). In most cases there is no evidence of intercurrent septic infection. There is insufficient evidence that diseased ovaries or parathyroids are factors. Osteomalacia may be prevented by increasing the vitamin and salt content of the diet, and may be cured by a sufficient diet plus a Ca activator such as cod liver oil and sunlight. In the area studied the incidence of the disease is from 1 to 3% of child-bearing women. It often commences at puberty though its effects are more often shown in pregnancy and the puerperium.

A. T. CAMERON

The amount of glucose, non-protein nitrogen, uric acid and total phosphorus in the blood of normal inhabitants of the tropics and of birds in avitaminosis. P. J. TEDINO VAN BERKHOUT. *Repts. Dutch-Indian Med. Civil Service* 4, 326-43(1924).—The composition of the blood of normal tropical men did not differ in glucose, non-protein N, uric acid or P from that of a normal individual inhabiting the temperate zone. A comparison of the blood of normal cocks with that of those fed on a diet deficient in vitamin B showed no change in the above constituents while with pigeons a hyperglucemia was usually manifest in the birds on the vitamin B-free food, the extent of which was not diagnostic of the extent of the avitaminosis.

H. J. DEUEL, JR.

Blood enzymes in experimental polyneuritis. A. KUDRYASHEVA. *Fermentforschung* 8, 177-80(1925).—Exptl. polyneuritis of pigeons is accompanied by disturbances in the enzymic functions of the blood. The serum from polyneuritic pigeons compared with that from normal pigeons showed a very slight decrease in diastatic activity, a considerable increase in lipolytic activity and a considerable decrease in proteolytic activity.

A. W. DOX

Origin and destiny of cholesterol in the animal body. XIV. Cholesterol metabolism in normal breast-fed infants. F. W. FOX AND J. A. GARDNER. *Proc. Roy. Soc. London* 98B, 76-92(1925).—During the early days of life (colostrum-meconium stage) the excretion of sterol exceeds the intake. During the transitional stage of lactation, the sterol balance of the infant shows either an equilibrium or a slight loss. As the age advances, retention of sterol occurs. The sterol present in the diet is a source of supply to the animal organism. However, some organ in the body must be capable of synthesizing an additional supply of cholesterol. Bile acids apparently are not derived from the cholesterol of the diet; and cholesterol and the bile acids probably are elaborated in the body by collateral processes.

JOSEPH S. HEPBURN

Researches on the fat nutrition of the nursing. UGO DE GIRONCOLI. *Pediatrics* 33, 579-601(1925).—G.'s oil-flour mixt consisting of 40 g milk, 60 g.  $H_2O$ , 5 g olive oil, 5 g flour and 3 g. sugar is clinically superior to the flour-butter soup of Czerny-Kleinschmidt. It can be fed to young infants and gives the best results when combined with a mixed diet. The individual tolerance to fats plays an important part in its effect. After a certain time intolerance develops, especially in summer. The expts. confirm the influence of fat on growth and Frontali's data relative to the absorption of olive oil in the nursing. The absorption usually increases with the age. M. J.

The most common Philippine fruits and vegetables suitable for dietetic treatment of diabetes. ISABELO CONCEPCION. *J. Philippine Islands Med. Assoc.* 5, 17-20 (1925).—Among the vegetables are lettuce, cucumber, tomato, papaya (green), fern (pako), celery, bottle gourd, sponge gourd, leek, Chinese mustard and cabbage. The fruits that may be used are melon, santol, papaya, pomelo, pineapple and orange.

FRANCES KRASNOW

The nitrogen efficiency of urea added to the food of young ruminants (goats). B. A. LAVROV, OLGA P. MOLCHANOVA, AND ANNA J. OCHOTNIKOVA. *Biochem. Z.* 153, 71-85(1924).—Young goats were fed hay, potato meal, sugar and urea. A positive N balance was maintained for the first periods of study, but as the goats grew the balance became negative until the amt. of urea in the diet was increased, when it became positive again. Respiratory quotients did not remain const. and tended to show a low protein utilization.

W. D. LANGLEY

Contribution to the biochemistry of avitaminosis. IV. Calcium separation and blood calcium in experimental scurvy. A. PALLADIN AND C. SRAWON. *Biochem. Z.* 153, 86-96(1924); cf. *C. A.* 19, 1727.—The Ca excretion of scorbutic guinea pigs decreased in most cases from about 17 mg. per 2 days excretion to about 12.8 mg. In the third week after the appearance of the scurvy it dropped to less than half the former value. Death then soon resulted. The decrease of Ca in the feces was less marked, while that per 5 cc. of blood fell from 0.625 to 0.439 mg. V. The metabolism in rabbits during a vitaminosis. A. PALLADIN AND A. KUDRIAWZewa. *Ibid* 154, 104-24(1924).—Vitamins A and C can be dispensed with by rabbits. In the absence of vitamin B (following rice feeding or autoclaved yeast) disturbed metabolism is evidenced by a hyperglucemia, increased urea, uric acid and  $NH_4$  excretion and increased creatine content of the muscles and an increased creatine coeff. with creatinuria. Mineral metabolism remains unchanged. A diminished neutral fat and cholesterol content of the blood and increased blood content of cholesterol esters, phosphatides and fatty acids follow feeding of polished rice to rabbits.

F. A. CAYORI

The influence of ultra-violet light upon accessory substances. I. The influence upon factor A. J. SPENKA. *Biochem. Z.* 153, 197-217(1924).—Mice were fed on a standard oat diet, and upon the same diet with added butter. The first group plainly showed the lack of vitamin A, and the second group showed it much less clearly. Irradiation of the butter caused death in 7 to 9 days, which was attributed not to the destruction of factor A, but to chemical changes in the butter. Irradiated differed from ordinary butter in taste and color, acidity, reducing power and in the Kreis and galium tests,  $n_D$ , and oxidation number. Volatile aldehydes, acids and phenols were present. The changes are due to the presence of  $O_2$ , for with air excluded, none occurred. The toxic substance could not be isolated from the irradiated butter. II. Influence upon factor B. *Ibid* 218-30.—Young pigeons were fed polished rice until they became polyneuritic. They were then treated with irradiated (20 min.) soles of vitamin B from yeast, and recovered from both the polyneuritic cramps and the alimentary dystrophy, which shows that vitamin B is not affected by ultra-violet light. III. Influence upon factor C. *Ibid* 231-7.—Guinea pigs kept upon a diet of oats developed scurvy. Concentrated lemon juice, which had been irradiated by ultra-violet light, cured them, whereas dil. juice (1:1), under the same conditions, failed to cure them. If the concd. juice was half neutralized to phenolphthalein, reconcd. to the original concn., and then irradiated, it failed to cure the guinea pigs. Therefore, citric acid seems to be a stabilizer of factor C. When the dil. lemon juice (1:1) was irradiated in absence of air, its antiscorbutic action was not destroyed. IV. Influence upon factor D. *Ibid* 238-41.—The growth factor D, when irradiated with a Hg-quartz lamp, is not destroyed either in the presence or absence of air.

W. D. LANGLEY

The development of white rats on a milk diet. E. FYUN. *Biochem. Z.* 153, 496-503(1924).—Rats grew better upon milk which had been quickly boiled than upon milk which had been pasteurized at 63° for 15 or 30 min. Upon skim milk to which previously boiled cream was added, the rats grew well, but upon boiled skim milk to which the same amt. of unboiled cream was added, they grew hardly at all. Milk

wh'ch had been treated with  $H_2O_2$  enabled growth of males to occur to a more marked extent than females, although reproduction was not interfered with. Similar expts. with guinea pigs and cats failed because of dietary difficulties. W. D. LANGLEY

Vitamin potency of cod-liver oils. XIII. Vitamin A potency of dogfish liver oil. A. D. HOLMES AND M. G. PIGOTT. *Ind. Eng. Chem.* 17, 310-1(1925).—The sp. gr. (0.9153 at 25°), d (1.4762), sapon. value (169.3), and free fatty acid value (0.261%) of dogfish liver oil were lower than those of codfish oil. Vitamin A studies with growing albino rats showed that 1 mg. of the oil contained sufficient vitamin A to supply the growth requirements of this species. H. B. LEWIS

Effect of high and low protein content on the digestibility and metabolism of dairy rations. A. E. PERKINS AND C. F. MONROE. *Ohio Sta. Bull.* 376, 85-116(1924).—In these expts. 8 cows, near their min. health wt. and producing large quantities of milk, were divided into 2 lots, one receiving high-protein and the other low-protein rations. The observed digestibility was lower in every case for each ingredient than that obtained by av. digestibility coeffs. This difference was greater for the low-protein rations. The cows receiving the high-protein rations consumed more  $H_2O$  and passed more urine than did the others. The excess of milk fat produced over that in the digested food was greater with the low-protein diet. All of the cows maintained or increased their wt. and positive N-balance and gave liberal amts. of milk, although half of them were receiving much less protein in their rations than is generally believed necessary for maintenance. Those fed high-protein rations stored Ca while the others excreted more than they consumed. The Ca and P balances obtained were much more favorable than those previously obtained under seemingly like conditions by other workers. Eighteen references, 29 tables and 8 illustrations are appended. A. L. MEHRING

By-products of wheat. Comparison of their biologic values as factors of maintenance, growth and fecundity. (MME.) L. RANDON, J. ALGUTER AND (MILLES.) ASSELIN AND CHARLES. *Compt. rend.* 179, 1342-5(1924).—Expts. with guinea pigs and with rats showed that these by-products considered as the single source of N have varying biologic values in a normal ration. The coarse bran and the very coarse flour are much inferior to the mixed bran and especially to the remilled bran. By the addn. of 10 to 30 g. of starch, 3 to 5 of Ca lactate, 8 of butter fat and 2 cc. of citron juice to 100 g. of coarse bran, maintenance of the guinea pig is not attained, but with the rat maintenance, growth and fecundity are attained, yet without the survival of the young. The addn. of gelatin to the coarse bran prolongs the life of the guinea pig but coincides in the rat with an arrest of reproduction. This indicated that the regular cycle of life is dependent upon a certain equil. between the amino acids of the food. If the gelatin is replaced by casein the litters are normal. Casein appears to contain some factor necessary for a normal fecundation and evolution of the embryo of the young, which factor is missing in coarse bran and in gelatin. L. W. RIGGS

Vitamin potency of cod-liver oil and other fish oils. E. POULSSON AND G. WEIDEMANN. *Tids. Kemi Bergs.* 5, 44-54(1925).—The vitamin potency is affected little or not at all by heating to nearly 100°, by neutralizing the free fatty acids with alkali, by bleaching and clarifying with fuller's earth or gently with steam, by the sex, age and state of spawning of the fish. The activity is easily destroyed by exposure to air and also by the more radical refining processes, such as hydrogenation. The nutrition conditions of the fish seem to be rather important, but generally they are very const. in the same regions. Very little difference was found in the vitamin potency in liver oils from the cod fish, haddock, coalfish, cusk, and ling. Similar activity was found in oils from rayfish and sharks, although the results along this line show less uniformity. The av. of 10 samples of different Norwegian oils as compared with the av. of 12 samples of different New Foundland oils show a difference in potency (in favor of the Norwegian oils) lying completely within the limits of experimental error. All the exams. mentioned concern the growth-promoting potency only. The anti-rachitic value has not been quant. examd. C. H. A. ROBAK

Studies of cod-liver oil and its characteristic taste. JOHAN HJORT AND AAGE LUND. *Tids. Kemi Bergs.* 5, 89-102(1925).—Oil spontaneously sepd. during the canning of fresh liver after storage in hermetically sealed containers for several months retained its full vitamin potency and had no disagreeable taste. This led to a series of expts. on the development of a technical process for the manuf. of tasteless cod-liver oil of full vitamin potency. App. and procedure are described in the Norw. pat. 40,210 (C. A. 19, 1354) and 40,792. A special after-filling device is necessary because of the contraction of the cooling oil in order to avoid the risk of a collapse of the barrel. However, the oil produced in this way and stored in sealed barrels for 4 months, while it had not turned rancid, tasted unpleasantly of liver and the foot had not kept fresh. Further

expts with different methods of eliminating the ill-tasting and putrefying components, such as bleaching, steaming and filtering, had only small success as regards the taste and keeping. The vitamin potency of the product, however, was in all expts normal or better than normal. A *whale oil* produced mechanically without heating showed a vitamin potency of about  $\frac{1}{3}$  to  $\frac{1}{2}$  of that of normal cod liver oil. A sample of a normal cod liver oil lost practically all of its potency after having taken up 10 cc. of  $O_2$  per g at  $100^\circ$ . Another sample was stored in an open bottle for 5 months and then showed only a very small effect in doses of 5 mg a day. A third sample stored for 5 months in vacuum in a sealed glass tube placed in a sunny window was wholly inactive in 10 mg doses. C. H. A. ROBAK

The oxidation of cod-liver oil. AAGE LUND *Tids Kemi Bergv* 5, 102-14(1925).—Rancidity is caused by oxidation. Other agents such as light, moisture and micro-organisms are not absolutely necessary to produce rancidity, nor are they (with the possible exception of light) sufficient when acting alone. Exposure to air will always produce rancidity. A convenient reaction for detecting beginning rancidity is the guaiacum reaction used by Vintilescu and Popescu (C. A. 10, 646). Various phenomena indicate the presence of an intermediate oxidation product of peroxidic nature, this being the substance producing the guaiacum reaction, which will always be found positive in oil subjected to the action of  $O_2$  even if it tastes "sweet" (not rancid). This peroxide during storage (even hermetically sealed) will be inverted into or promote the formation of ill-tasting substances. If the oil contains cellular tissues from the raw material the rancidity will not occur as quickly as in refined oil, a fact ascribed to a reducing effect of the tissues destroying the peroxide. The oxidation processes were examd directly by absorption expts at  $100^\circ$  in a special app. An expt. with pure olive oil gave a curve corresponding well to the logarithmic curve of an autocatalytic reaction. The expts with cod-liver oil gave similar curves, a little more complicated, however, because of the peculiar nature of this material. The process of oxidation may be divided in 2 periods, the inductive (the slowly rising part of the curves) and the logarithmic one (the steep part). A small amt of liver added to the oil increased the inductive period markedly, this was also the case with other reductives such as pyrogallol, which latter retarded the absorption very noticeably when added in amts of 0.01%. Varnish, which gives a very strong guaiacum reaction, added in an amt. of 3.4% reduced the inductive period to zero. In the logarithmic period of oxidation the oils give a strong guaiacum reaction but during the inductive period the reaction is only faint. The catalytic substance is not identical with the rancid-tasting substances, since a rancid oil which had been stored for a long time in a sealed container showed a very long inductive period, the catalyst having been eliminated during the storage. The guaiacum reaction was negative. The catalyzing mechanism is explained in accordance with Tschirch and Barben (C. A. 18, 2976). If 1% of cod liver oil is added to margarine it will at first do no harm to its flavor but rancidity will occur much more quickly than in unmixed margarine, the oil acting as a catalyst. This effect was shown by expts with addn. of small amts. of cod liver oil to pure olive oil; the inductive oxidation period was considerably reduced. C. H. A. ROBAK

Relation between the diet, the composition of the blood and the secretion of milk of dairy cows. C. A. CARY AND E. B. MEIGS *J. Agr. Research* 29, 603-24(1924).—Sharp reductions in the quantity of energy in the ration of a milk cow or in either the quantity or quality of the protein are immediately followed by reductions in milk yield and by a change in the compn of the milk. When the original ration is again substituted for the reduced ration there is a general tendency for the yield and compn of the milk to return to their original status. These changes in the rations and milk along with those found occurring simultaneously in the amino N, tryptophan and other blood constituents detd in these expts suggest the view that the changes in dietary protein and energy affect milk secretion largely by inducing changes in the quantity and quality of the amino-acid mixt. circulating in the blood plasma. W. H. ROSS

Effect of phosphatides (lecithins) upon metabolism. ERICH HESSE. *Arch. expl. Path. Pharm.* 105, 185-207(1925).—When administered to mice and rabbits phosphatides cause a deposition of fats, because of a stimulation of fat formation from carbohydrates. Administered to man hydrolecithin causes a very considerable gain in wt. G. H. S.

Changes in the protein exchange due to acid administration. RAGNAR BERG. *Arch. expl. Path. Pharm.* 105, 218-9(1925).—Criticism of certain statements made by Geil (C. A. 18, 2365). G. H. S.

## F—PHYSIOLOGY

ANDREW HUNTER

Energy utilization in typewriting. HERMANN SCHROETTER *Arch. ges. Physiol. (Pflüger's)* 207, 323-42(1925).—Under ordinary conditions in typewriting, striking about 400 keys per min., the  $O_2$  utilization amounts to approx 180 cc per min., an excess of 50 cal. and an external work performance of 5000 m kg. Under favorable conditions these values may increase to 80 cal and 7800 m kg. G. H. S.

Investigations on blood platelets. G. BIANCHINI *Arch. ital. biol.* 73, 11-8(1924); cf. *C. A.* 17, 3366.—Platelets from blood of normal animals agglutinate dilns of serum which are unaffected by platelets from blood of asphyxiated animals. A. T. C.

Preexistence of platelets in the circulating blood. B. POLETTINI *Arch. ital. biol.* 73, 39-51(1924).—Staining methods show that platelets preexist in the normal vessels of normal mammals, and can be distinguished from alteration and disintegration products, natural or artificial, of other hematic elements. A. T. CAMERON

Hyperplasia of muscular tissue of the uterus of female rabbits in rut. O. ANDREI *Arch. ital. biol.* 73, 52-4(1924).—The hyperplasia is manifested by the presence of mitosis, and is probably due to the presence of sp. substances in the circulating blood at this period, since such blood injected into the circulation of animals not in rut causes proliferation of the uterine fibro-cells, even, apparently, in females that have not attained sexual maturity. A. T. CAMERON

The significance of glycogen in embryonic life. G. VASTARINI CRESI. *Arch. ital. biol.* 73, 97-107(1924).—Epithelial cells in the embryo previously described as clear, or vesicular, are in reality surcharged with glycogen. Glycogen infiltration has been demonstrated as an organogenetic factor in the mouth and rectum, the larynx, urethra, prepuce and vagina, nares, pupils and lachrymal canals, and the canalization of the acoustic meatus. A. T. CAMERON

The average amounts of uric acid and urea in the bloods of birds. G. PUPILLI. *Arch. ital. biol.* 73, 181-6(1924); cf. *C. A.* 18, 2193.—Results for several species are in general agreement with those previously published for fowls. A. T. CAMERON

The actual reaction of blood serum of birds. M. ISALBERTI *Arch. ital. biol.* 73, 157-60(1924).—Av. results for 25 fowls and 4 carnivorous birds (4 species) were  $pu$  7.09, the extremes observed being 6.65 and 7.57, all values measured at 22°. A. T. C.

Mechanism of insulin hypoglycemia. V. DUCCESCHI *Arch. ital. biol.* 74, 107-16(1924).—The velocity of absorption of glucose in the abdominal cavity of rabbits for solns. contg. between 0.25 and 0.75 g % is markedly greater when these contain insulin; in this case there is also diffusion of a larger amt of  $H_2O$ . With increased concns. the differences become less marked. The phenomena can be explained by diffusion and osmosis. A. T. CAMERON

Influence of glucosamine on insulin hypoglycemia. Possibility of transformation of glucosamine into glucose in the organism. A. MOSCHINI *Arch. ital. biol.* 74, 117-25(1924).—Glucosamine-HCl produces no effect on insulin hypoglycemia when injected subcutaneously, but produces favorable action when given by stomach tube either at the same time or a little before an insulin injection. This suggests that part of the glucosamine is transformed into glucose. Cf. following abstr. A. T. C.

Action of some mono- and disaccharides administered by stomach tube on insulin hypoglycemia. A. MOSCHINI *Arch. ital. biol.* 74, 126-30(1924).—Symptoms of insulin hypoglycemia in rabbits are relieved by stomach tube administration most rapidly by glucose, almost as rapidly by fructose, sucrose, or maltose, very little by galactose, which only exerts an action when introduced 2 or 3 hrs. before insulin injection, and not at all by lactose. Since except glucose these sugars are inactive when injected, their beneficial action must depend on transformation into glucose and its degree on the rate of such transformation. A. T. CAMERON

Mechanism of insulin action. G. VIALE *Arch. ital. biol.* 74, 131-40(1924).—Insulin *in vitro* does not act on glucose, either in absence or presence of ext. of liver or muscle. Ultrafiltrates of normal blood, diabetic blood, and venous blood from the pancreas show the same ratio between reducing and rotation power. Insulin does not affect the glucolytic scission of *saccharomyces*, nor the glucolysis of defibrinated blood. Action of the pancreas on glucolysis does not depend only on insulin, but is more complex. After injection of insulin  $HCO_2H$  increases in the blood. Following pancreas removal, it diminishes, and injection of insulin into the diabetic animal results in an increase, whence V. concludes that the acid is derived from glucose, through the action of insulin. A. T. CAMERON

Influence of insulin on hepatic glycogen. D. BINDI. *Arch. ital. biol.* 74, 141-5

(1924).—Using simple and double artificial perfusion of the surviving liver of the dog, B. finds that the presence of insulin in the circulation markedly diminishes the concn. of glucose in the liquid leaving the liver, indicating inhibition of glycogen hydrolysis. Lobes of liver irrigated by blood contg. insulin retain more glycogen than those in which glycogen has not circulated. In livers denuded of glycogen, as in the depancreatized dog, presence of insulin in the circulating blood detcs. conversion of part of the circulating glucose into glycogen.

A. T. CAMERON

The problem of the fundamental action of insulin. J. J. R. MACLEOD. *Can. Med. Assoc. J.* 15, 476-8(1925).—"So far as available evidence goes, we have no clue as to what becomes of the sugar which disappears in such large amts. following the injection of insulin."

A. T. CAMERON

The effect of pituitary preparations on the nitrogen metabolism. J. P. GRABFIELD AND A. M. PRENTISS. *Endocrinology* 9, 144-9(1925).—No effect on the level of the urinary N or of the non protein N of the blood in patients on a const. N intake resulted from the intramuscular injection of pituitrin or from the oral administration of prepus. of the anterior or posterior lobe or of the whole gland.

H. J. DEUEL, JR.

Muscular exercise, lactic acid, and the supply and utilization of oxygen. IX. Muscular activity and carbohydrate metabolism in the normal individual. K. FURUSAWA. *Proc. Roy. Soc. London* 98B, 65-76(1925); cf. *C. A.* 19, 673.—The respiratory quotient (R. Q.) does not reveal what substance is undergoing oxidation in the muscle itself during exercise. On a normal diet, the av. value of the R. Q. due to a short element of exercise is 1.01; and only carbohydrate is responsible for the processes of contraction and recovery. As exercise is prolonged, the R. Q. of the excess metabolism slowly decreases, showing that some substance other than carbohydrate is undergoing oxidation. On a fatty diet, even when the basal R. Q. reaches 0.71, short lived muscular exercise is performed at the expense of carbohydrate alone. If the exercise be prolonged, fat is used more quickly than on a normal diet. Conclusion: In exercise of short duration with no change in the general metabolism of the body as a whole, the body acts as an isolated muscle in which only carbohydrate is oxidized. Therefore, the primary fuel of contraction in human muscle is carbohydrate; fat and protein are presumably used to replenish the carbohydrate store.

JOSEPH S. HEPBURN

The inner secretion of the pancreas. A. I. KUSNETZOW. *Z. ges. expil. Med.* 45, 114-29(1925).—Ringer-Locke soln. that has passed through an isolated pancreas contains the inner secretion of the pancreas, the so-called pancreotoxin. It has a weak vasoconstrictor effect on peripheral vessels and a barely perceptible effect on vessels of the internal organs. Pancreotoxin inhibits the action of the fresh isolated heart but stimulates a tired heart. There is an antagonistic action between the internal secretions of the adrenals and pancreas. Pancreotoxin passed through an isolated adrenal increases the elimination of the active principle. The pancreas has an important role in sugar metabolism and its internal secretion increases the resorption of sugar by an isolated heart and diminishes the blood sugar content of normal animals though it has no effect on glucolysis *in vitro*. The vessels of the pancreas react to vasoconstrictor and vasodilator toxins less strongly than do the vessels of other organs.

H. F. H.

The inner secretion of the isolated thyroid gland. G. L. SCHAWERA AND L. P. KOTSCHERGIN. *Z. ges. expil. Med.* 45, 143-53(1925).—Ringer-Locke soln. passed through an isolated thyroid gland contains its inner secretion. This has a weak vasoconstrictor effect, has no effect on blood pressure but causes increased action in an isolated heart in rapidity of rhythm and in amplitude of contraction. In strong concn. the inner secretion of the thyroid increases the secretion of an adrenaline-like substance by the isolated adrenal. The vessels of the isolated thyroid respond to vasoconstrictor and vasodilator substances such as adrenaline and caffeine.

HARRIET F. HOLMES

General endocrinology and the teeth. WM. G. WARD. *Am. Med.* 31, 224-9(1925).—A general discussion.

FRANCES KRASNOW

The change of nitrogen and chlorine excretion in the urine with change of relations between blood and tissues. S. TAKANOSU. *Biochem. Z.* 153, 242-52(1924).—By feeding rabbits a const. diet of milk and bread, the N excretion was maintained for a time between 0.61 and 0.77 g., and the Cl excretion between 0.75 and 1.1 g. per day. Blood was then removed (35 cc. from a 1.8 kg. rabbit) and changes in body wt., urine vol., N and Cl excretion, and hemoglobin were followed. N, Cl and hemoglobin all decreased, but the Cl soon increased again, while N remained low. Successive pituitrin injections were then made, causing a decreased flow of urine, and a lowered N and Cl excretion.

W. D. LANGLEY

Enzymes of the skin. II. J. WOHLGEMUTH. The distribution of enzymes in the skin, and the occurrence of nucleotidase. E. KLOPSTOCK. *Biochem. Z.* 153,

487-95(1924); cf. C. A. 19, 84.—In addition to the enzymes previously found in skin, there are now shown to be present trypsin and a nucleic acid-splitting enzyme, which occurs in the soles of the feet. Lipase and phenolase are most plentiful in the skin of the genital organs. W. D. LANGLEY

The resistance of immature erythrocytes to heat. R. ISAACS, B. BROCK AND G. R. MINOT. *J. Clin. Invest.* 1, 425-33(1925).—Immature erythrocytes of both normal and pathological blood are more resistant to heat—30 min. at 55°—than mature erythrocytes. The difference is purely quant. The younger of the mature cells are probably more resistant to heat than the older ones. LOUIS LEITER

The plasma proteins in relation to blood hydration. I. J. P. PETERS, A. J. EISENMAN AND H. A. BULOCH. *J. Clin. Invest.* 1, 435-50(1925).—Changes in plasma vol., as produced by oxalating the blood, varying  $\text{CO}_2$  and  $\text{O}_2$  tension, venous stasis, exercise, hydermia, etc., are reflected fairly closely in the concn. of plasma proteins. When blood is drawn under standard conditions in a normal individual, the plasma protein level is quite const. over a period of 2 years. Normal plasma proteins were found in patients with arteriosclerosis and hypertension, severe acute infections, disease of the liver, and in some cases of severe anemia. LOUIS LEITER

Calcium excretion through the bile. E. GILLEY. *Z. ges. expil. Med.* 43, 539-44(1924).—The bile is an instrument for Ca excretion in that it excretes  $\frac{1}{2}$  of the amt. excreted by the urine. The concn. of Ca excreted by the bile does not depend upon that excreted by the urine, but is a function of the liver. F. B. SEIBERT

The so-called anion deficit of blood serum. Determination of the dissociation constant and of the concentration of unknown acids in the serum. RUDOLF MOND AND HANS NETTER. *Arch. ges. Physiol.* (Pflüger's) 207, 515-22(1925).—The assumed union of alkali to the serum proteins is unwarranted; the occurrence of a deficit in anions and osmotic active substances suggests the existence of a hitherto unknown acid (or acids). Electrometric detns. upon ultrafiltrates of beef serum reveal the presence of such an acid (or a mixt. of acids) having a dissociation const. of  $10^{-3.2}$ , and present in a concn. of N/70 to N/120. G. H. S.

## G—PATHOLOGY

### H. GIDEON WELLS

Metabolism of carcinoma cells. O. WARBURG, K. POSENER AND E. NEGELEIN. *Biochem. Z.* 152, 209-44(1924).—By Warburg's manometric method (C. A. 19, 1720) the O and  $\text{CO}_2$  respiration, and anaerobic and aerobic glycolysis of human malignant and benign tumors and Flexner-Jobling rat carcinoma were measured and compared with like measurements of normal cells of muscle and glands. The aerobic glycolysis-respiration ratio of benign tumors is  $\frac{1}{2}$  to  $\frac{1}{4}$  of the same ratio in malignant tumors, so that 3 to 4 times as much lactic acid is formed in the malignant cells as in the benign. F. A. CAJORI

Properties of purified Dick scarlatinal toxin. F. M. HUNTOON. *Proc. Soc. Exptl. Biol. Med.* 21, 513-4(1924).—The toxin is pptd. by  $(\text{NH}_4)_2\text{SO}_4$  in concn. of 70-75%. When this fraction is purified, 75% of the toxicity is retained, the substance is almost free of N, it is destroyed by trypsin and by heating at 90° for 1 hr. C. V. B.

Increased gastrointestinal permeability as a possible factor in parathyroid tetany. A. B. LUCKHARDT AND E. L. COMFERE. *Proc. Soc. Exptl. Biol. Med.* 21, 523-6(1924).—Parathyroidectomized animals developed tetany following the administration of cathartics; the symptoms disappeared when calcium salts, excepting  $\text{CaH}_2(\text{PO}_4)_2$ , were given. C. V. B.

Ketosis associated with conditions of alkalosis. L. E. BOOHER AND J. A. KILLIAN. *Proc. Soc. Exptl. Biol. Med.* 21, 528-9(1924).—Abnormally large quantities of ketone bodies were found in the blood associated with uncompensated alkalosis due to alk. therapy or to loss of HCl through vomiting. Values for acetone of the blood of 60, 50, 66, 28, and 8 mg. per 100 cc. were found associated with  $\text{pH}$  values of 7.58, 7.54, 7.50, 7.52, and 7.50, resp. The bicarbonate contents of these bloods were 84, 83, 88, 87, and 70, resp. Acetone was excreted in large quantities in the urine. C. V. B.

Effects of dehepatization on the reactions of the urinary bladder in canine anaphylactic and histamine shock. W. H. MANWARING, V. M. HOSEPIAN, J. R. ENRIGHT AND D. F. PORTER. *Proc. Soc. Exptl. Biol. Med.* 21, 538-7(1924).—During the first 2 min. of canine anaphylactic shock, the urinary bladder is thrown into sharp contraction. Intravenous injection of histamine has the same effect. In dehepatized dogs, the anaphylactic bladder reaction cannot be elicited; the histamine reaction persists.

Possibly the bladder reaction is produced in canine anaphylactic shock by the liberation of a substance from the liver having a histamine-like action. C. V. B.

Production of goiter in rats by restricted iodine feeding. E. M. HAYDEN, W. T. WENNER AND C. W. RUCKER. *Proc. Soc. Exptl. Biol. Med.* 21, 546-7(1924).—The thyroid glands of rats deprived of  $I_2$  weighed twice as much as the glands of rats receiving  $H_2O$  contg. 0.1 mg. of  $I_2$  per l. C. V. B.

The reticulo-endothelial system in relation to antibody formation. F. P. GAY AND A. R. CLARK. *Proc. Soc. Exptl. Biol. Med.* 22, 1-3(1924).—Rabbits and rats were repeatedly injected with trypan blue for about 2 wks. and then given 3 injections of sheep blood cells on successive days. Control rats showed hemolysis in dilns. of 1-2500 to 1-10,000, 2 test rats were negative at 1-10, and 2 others showed no hemolysis beyond 1-160. In control rabbits the hemolysis titer averaged 1-1666 in 9 days; the max. production in trypan blue rabbits was 1-140 after 14 days. Possibly the colloidal dyestuff "plugged" the cells of the reticulo-endothelial system and prevented antibody formation. C. V. B.

Acidosis in rarified air. G. VIALE. *Arch. ital. biol.* 74, 40-50(1924).—See C. A. 18, 2375. A. T. CAMERON

Cholesterol in cases of gall-stone formation. K. ENGEL AND S. CIERMA. *Wien. klin. Wochschr.* 38, 122(1925).—Increasing the blood-cholesterol content by prolonged intraperitoneal injections of cholesterol emulsions failed to give rise to gall-stone formation in guinea pigs. This is contrary to the accepted theory that in humans increased blood cholesterol is significant in gall-stone formation. W. F. GOEBEL

The lactic acid content of blood under normal and pathological conditions. III. Administration of glucose. A contribution to our knowledge of diabetes. BRUNO MENDEL, WERNER ENGEL AND INGEBORG GOLDSCHNEIDER. *Klin. Wochschr.* 4, 542-4(1925); cf. C. A. 19, 2079.—Administration of glucose to a normal resting person leads to the well known transitory hyperglucemia, but the lactic acid content of the blood remains unchanged, which shows that the glucose that disappears so rapidly from the circulation is not oxidized. It must be stored in the body cells as such. In diabetics, the glucose is unable to permeate the body cells. IV. Lactic acid content of blood after treatment with insulin. *Ibid.* 804-6.—The lactic acid content of blood from normal or diabetic, resting individuals is not changed after injecting insulin. (Subjects were fasting or had just ingested large amts. of carbohydrate.) Blood sugar was markedly reduced in every case; but the sugar had, obviously, not been oxidized. Insulin is not directly involved in the oxidation of carbohydrates. It produces some change in body tissue that enables the latter to bind glucose in such a way that the glucose can be oxidized. The glucose is not stored as glycogen. MILTON HANKE

The metabolism of carcinoma cells. OTTO WARBURG. *Klin. Wochschr.* 4, 534-6(1925).—Carcinoma cells not only oxidize glucose but they convert (glucolysis) a large part of it into lactic acid (10-12% of their own wt. per hr.). This differentiates them sharply from embryonic tissue and from resting and active epithelium. The metabolism of carcinoma cells is predominantly glucolytic, subordinately oxidative. The reverse is true of normal body cells. MILTON HANKE

Insulin and increase in body weight. J. ST. LORANT. *Wiener Arch. inn. Med.* 9, 409-18(1925).—The rise in weight in diabetics after insulin treatment is not due to  $H_2O$  retention alone. The curves for  $H_2O$ , salts and N balance run parallel, indicating that there is a causal relation between them. HARRIET F. HOLMES

Pathology and therapy of mountain sickness. II. D. A. ADLERSBERG AND O. PORGES. *Z. ges. exptl. Med.* 45, 166-207(1925).—Persons unaccustomed to high altitudes show a decreased O satn. of the blood or hypoxemia. Those accustomed to the altitude show an increased  $CO_2$  tension in the alveolar air and a less degree of O satn. in the blood. Administration of  $NH_4H_2PO_4$  causes better accommodation in respiration in high altitudes. There is a lessened  $CO_2$  tension and an increased O tension in the alveolar air and a greater degree of O satn. in the blood, confirming lab. expts. II. F. H.

Blood calcium studies. VII. Action of intravenous calcium injection on the organism. E. KYLIN AND G. NYSTRÖM. *Z. ges. exptl. Med.* 45, 208-16(1925); cf. C. A. 19, 2080.—The reactions following intravenous Ca injections closely parallel the reactions caused by injections of adrenaline. There is a rise in blood pressure and in sugar content of the blood, and an increase in white blood cells, chiefly polynuclears. Both Ca and adrenaline injections in certain conditions cause a fall instead of a rise of blood pressure. HARRIET F. HOLMES

Experimental study of kidney pathology with help of indirect vital staining methods. I. L. PAUNZ. *Z. ges. exptl. Med.* 45, 234-45(1925).—After intravenous injection in animals of a sulfonic acid dye, such as water blue, the dye is changed to the colorless

carbinol form and is eliminated in the urine in that form in a short time and is also deposited in the cells of the convoluted tubules of the kidney in granular form, at first as colorless and then colored granules. When passive congestion is induced, elimination of the dye is not interfered with but it is not deposited in the cells in granular form, indicating that the 2 processes are independent of each other. HARRIET F HOLMES

The clinical importance of the phosphates of the blood with particular regard to the healing of fractures. P GYÖRGY and E SULGER. *Z ges expil Med* 45, 224-33 (1923).—The P content of the blood, which normally averages 3 mg., rises usually to 5.9 mg. during the healing of fractured bones, returning to normal after consolidation takes place. When the fracture fails to heal the P content of the blood does not rise. In children the P content is normally high, but increases during the healing of fractures. There is a P increase after osteotomies but not after operations on the soft tissues of the body. The rise in P content in normal fractures shows a seasonal variation, being most marked in the spring months. Goiters accompanied by thyreotoxic symptoms show a P increase. HARRIET F HOLMES

Photochemical serum reactions and their colloidal chemical foundation, with particular references to the Kottmann reaction. F PELTASON. *Z ges expil Med* 45, 246-66 (1925).—With the use of Kottmann's photochem method (*Schweiz med Wochschr.* 50, 644 (1920). cf. *C A* 14, 2370) with slight modification, 105 blood sera were examined. K.'s findings were substantiated in the main, but the differences found were too small to be of practical clinical value. It is not, as K. maintained, a sp colloidal action of I on iodocolloids, for similar results may be obtained with AgBr. Artificial sols, as gelatin or casein, whose degree of dispersion is altered by changes in pH, show a distinct connection between the degree of dispersion of the material and the sensitivity to light in the Kottmann reaction. A new method for estg relative degrees of dispersion may be worked out along this line. HARRIET F HOLMES

A contribution to the study of the chemical composition of normal and luetic serums and the determination of colloidal and non-colloidal nitrogen. A A SOLARI. *Rev. facultad cienc quim.* 3, 1-63 (1925); *Anales asoc quim Argentina* 12, 421-32 (1924).—The Bordet-Wassermann test should be carried out with the fresh as well as with the inactivated serum. For the former the modification of Ronchese and Mathis-Laboulle, for the latter that of Ronchese and Millet is recommended. The  $Al(OH)_3$  for the pptn. of the proteins, according to Welker and Falls, should be prep'd from 1% sols of pure reagents under exactly the same exptl. conditions. Slight adsorption by  $Al(OH)_3$  was observed at least in very dil. urea and  $(NH_4)_2SO_4$  sols. It does not follow the rule of Freundlich and does not affect the results. Abderhalden's modification of the micro-Kjeldahl and Folin methods has no advantage over the original methods for N in quantities over 14 mg. The investigation of 62 serums shows that the colloidal and non-colloidal N content and their ratio varies within the same limits in luetic and non-luetic serums. MARY JACOBSEN

Optical activity of glucose as influenced by normal and diabetic urines. J. R. PAUL. *J. Clin. Invest.* 1, 317-31 (1925).—Diminution of *l*-rotation of dil. normal urine occurs on standing, zero being reached in 3-5 hrs., with a return to initial values in 24 hrs. Similar, but more irregular, changes occur in dil. diabetic urine. Addition of 1% glucose to normal and diabetic urines shows only slight quant. differences between the two. LOUIS LEITER

The deposition of calcium phosphate and calcium carbonate in bone and in areas of calcification. J. C. WATT. *Arch. Surg.* 10, 982-90 (1925).— $Ca_3(PO_4)_2$  and  $CaCO_3$  show easily identified shapes of particles when ppt'd in colloids. The salts are not present as discrete particles in bone and show no evidence of simple pptn., but are apparently secreted by the osteoclasts. The direction of travel of Ca from blood to bone can be reversed. In calcification the same salts are present as those in ossification and in the same proportions, but are apparently deposited by pptn. JOHN T MYERS

The toxin content of diphtheria toxin. RICHARD PRIGGE. *Centr. Bakt. Parasitenk.* 1 Abt., Orig. 92, 39-40 (1924). JOHN T MYERS

The conception of anaphylactic shock as a physicochemical phenomenon. Basis of the metabolic dispersion theory. I. L. KRICHEVSKII. *Centr. Bakt. Parasitenk.* 1 Abt., Orig. 92, 277-308 (1924).—The metabolic dispersion theory postulates as the cause of anaphylactic shock in living organisms, changes in the degree of dispersion of colloids in the blood but especially in cell protoplasm. The theory is based on changes in compn. and  $pH$  of blood after shock, on changes in the degree of dispersion of blood colloids, and on the histological demonstration of increase or decrease in the dispersion of cell protoplasm. The theory considers every cell a microscopic test tube filled with colloid. The action of antigens and antibody changes the condition of colloidal aggre-

gates, resulting in cell destruction. This is analogous to ppto., agglutination, or hemolysis, in the macroscopic test tube. Physicochem. agents, the antigen in sensitized organisms, act directly on the cell rather than producing toxic substances. The theory avoids the use of the term poison, not because the products of changed degrees of dispersion could not be called poisons, but because the term is usually applied to substances with a fixed specific chem. action.

JOHN T. MYERS

Observations on the decrease of potency of precipitating serum. H. BEGER. *Centr. Bakt. Parasitenk. 1 Abt., Orig. 92, 308-12* (1924).—When pptg. serum stands in containers of poor glass, its power decreases because of alkali going into soln. J. T. M.

Titration of antitoxic sera in vitro, especially tetanus antitoxin. W. SHOLZ. *Centr. Bakt. Parasitenk. 1 Abt., Orig. 92, 434-8* (1924).—Tetanus toxin and antitoxin will flocculate like diphtheria toxin and antitoxin. It is possible that a method adapted to commercial use can be devised.

JOHN T. MYERS

Serum color reactions. FELIX KLOPSTOCK. *Centr. Bakt. Parasitenk. 1 Abt., Orig. 92, 572-4* (1924).—Oxazine and thiazine can be reduced to their leuco bases by serum and reoxidized to the dye by the air. Most of the triphenylmethane dyes can be so reduced and reoxidized. This occurs with either normal or diseased serum.

JOHN T. MYERS

The question of the erythrocyte membrane. O. B. LEPESECHINSKAJA, *Folia Hematol. 31, 87-108* (1925).—The erythrocyte has a membrane which preserves its form. It is not an artifact but is produced by the cell. It stains with basic dyes and its contents stain with acid dyes. It consists of fibrinogen and lipoids; hence it is pptd. by tannin and  $HgCl_2$ , and is sol. in weak alkalis, acids and neutral salts. An increase of body temp. may change the colloidal state of the membrane and increase its permeability, thus explaining increased respiration and heart rate in fever.

JOHN T. MYERS

The volume and hemoglobin content of the erythrocytes in health and disease. R. L. HADEN. *Folia Hematol. 31, 113-35* (1925).—The satn. index of erythrocytes is obtained by dividing the hemoglobin in percent by the vol. percent of cells. In newborn infants the vol. and color index are high. In normal adult blood the vol. of the ev. red cell is  $9.6 \times 10^{-11}$  cc, the hemoglobin content  $3.12 \times 10^{-11}$  g, and the hemoglobin percentage 32.5. In 50 cases of pernicious anemia the av. vol. index was 1.41, the color index, 1.29, and the hemoglobin satn. index 0.92. In 47 cases of hemolytic secondary anemia, the av. vol. index was 0.94, the color index 0.81, and the satn. index 0.81. In 8 cases of chronic hemorrhagic secondary anemia the av. vol. index was 0.77, the color index 0.62, and the hemoglobin satn. index 0.80. The % hemoglobin is nearly as high per unit vol. of cells in secondary as in primary anemia; the difference is in the size of the cells.

JOHN T. MYERS

Experimental soot cancer. R. D. PASSEY AND J. CARTER-BRAINE. *J. Path. Bact. 28, 133-44* (1925).—An active fraction was made from soot consisting mainly of ether-sol. bases, which will produce cancer in mice. On further fractionation, carcinogenic fractions distil over above  $190^\circ$  at 20 mm. Hg pressure.

J. T. M.

The influence of the fat-soluble accessory food factor upon the initiation of soot cancer in mice. R. D. PASSEY AND J. L. WOODHOUSE. *J. Path. Bact. 28, 145-6* (1925).—Fat-sol. A has no effect on the induction of cancer by soot.

J. T. M.

Correlation coefficients of the urine with special reference to cancer. C. W. WHITE. *J. Path. Bact. 28, 211-31* (1925).—Four thousand coefficients were detd. Urea is correlated chiefly with creatinine,  $H_2PO_4$ , K and acidity; creatinine with K, Na, chloride and water, uric acid with phosphate, acidity and sometimes with Ca; sulfate with Mg and K; phosphate with K, Ca and Mg; chloride with Na and K. The chief alk. phosphates are those of Na and Ca and the chief acid phosphates K, Ca and Mg. Na and Cl show a high correlation with water.

JOHN T. MYERS

The measurement of the combining power of diphtheria toxin and toxoid with antitoxin in relation to their antigenic efficacy. A. T. GLENNY, C. G. POPE AND HILDA WADDINGTON. *J. Path. Bact. 28, 279-303* (1925).—The combining power of a toxin can be fully detd. by the flocculation test. Antitoxin has a greater affinity for toxin than for toxoid. Toxin and antitoxin can dissociate from combination. Both toxin and toxoid are antigenic.

JOHN T. MYERS

The effect of serum-sensitiveness and *gossypitin* formation upon the efficacy of diphtheria toxoid and toxin-antitoxin mixtures in promoting antitoxin production. A. T. GLENNY, BARBARA HOPKINS AND HILDA WADDINGTON. *J. Path. Bact. 28, 305-15* (1925).—Precipitin formation prevents the antigenic action of toxin-antitoxin mixt., and has an inhibitory effect on the antigenic power of toxoid.

JOHN T. MYERS

The titration of diphtheria toxin by the flocculation method. A. T. GLENNY AND U. WALLACE. *J. Path. Bact. 28, 317-31* (1925).—Ninety % of the tests made were

correct within 10%. A rough detn. of the strength of a toxin can be made in 30 min. Cf. C. A. 19, 1735. JOHN T. MYERS

Blood urea and its estimation in diabetes mellitus. C. E. BRUNTON. *Quart. J. Med.* 18, 241-9(1925).—Twort and Archer's method for the detn. of blood urea is very satisfactory. There is no relation between the quantities of blood sugar and urea in diabetes. Insulin does not alter the blood urea concn., and the duration of diabetes does not necessarily increase its concn. High blood urea does not always accompany diabetic coma. JOHN T. MYERS

Changes in the blood in anesthesia. DOROTHY G. E. POTTER. *Quart. J. Med.* 18, 261-73(1925).—During anesthesia there is a decrease in the alk. reserve. When a rise in blood phosphate occurs it is due to the inorg. radical; the rise in the hydrolyzable and total acid-sol. fractions is due to the inorg. portion being included in the latter. It may be that a hexose-phosphoric acid compd. passes from muscles to blood. Also the excess of phosphate in the liver may be mobilized to permit renal excretion of acids. JOHN T. MYERS

The tolerance of the body for urea in health and disease. H. E. ARCHER AND G. D. ROBB. *Quart. J. Med.* 18, 274-87(1925).—The patient drinks 15 g. of urea 3 hrs. after a breakfast of tea and toast. Specimens of blood and of urine are taken after 30, 60, 120 and 240 min. and urea detns. made. In the normal individual the rise in blood urea is 5 to 15 mg. in 30 to 60 min. Recovery is complete in 120 min. The test detects azotemic renal deficiency which is missed by the concn. test and the single estn of urea. The urea level in such instances will go much higher and the recovery will be much slower. JOHN T. MYERS

Calcium and magnesium in some pathological sera. ELSIE WATCHORN. *Quart. J. Med.* 18, 288-93(1925).—In a variety of chronic infections the serum Ca and Mg were increased sometimes as much as 30%. There was no relation between the variations in Ca and Mg. JOHN T. MYERS

The relation of infection to diabetic coma. GEORGE GRAHAM. *Quart. J. Med.* 18, 294-9(1925).—Insulin is much less effective in lowering the blood sugar in diabetic coma if an infection occurs. JOHN T. MYERS

The spinal-fluid sugar in encephalitis. J. L. HALLIDAY. *Quart. J. Med.* 18, 300-8(1925).—Fasting blood sugar curves are not diagnostic. The fasting level of the spinal fluid sugar is lower than that of the blood sugar. The spinal-fluid sugar curve is like the blood sugar curve except that it is delayed. JOHN T. MYERS

Carbohydrate tolerance in myxedema. H. GARDINER-HILL, P. C. BRETT AND J. F. SMITH. *Quart. J. Med.* 18, 327-34(1925).—In exophthalmic goiter there is a tendency to glucosuria and high and prolonged blood sugar curves. In myxedema the renal threshold is raised. The blood sugar is high but there is no glucosuria. JOHN T. MYERS

Pituitary obesity in adolescence. H. GARDINER-HILL, I. JONES AND J. F. SMITH. *Quart. J. Med.* 18, 309-26(1925).—Obesity develops concurrently with over-growth. In the early stages there is an inability to use carbohydrates, and in the late stages an increased sugar tolerance, which is due to increased power of storage not to increased oxidation. This may be due to a hyperactivity of insulin, because of a lack of the normal controlling pituitary hormone. JOHN T. MYERS

Chemical constitution of normal and of pathologic crystalline lens. H. LABBÉ AND F. LAVAGNA. *Compt. rend.* 180, 1186-8(1925).—Analyses of normal and of cataract crystalline lenses gave the following figures, resp.: water 65.23, 71.50; total N 15.54, 10.62; N of the sol. albumin 4.36, 1.37; total formol-titratable N 2.49, 2.60; formol amino N 0.34, 1.34. L. W. RIGGS

Sugar threshold in 100 cases of diabetes. J. H. ROE AND O. J. IRISH. *J. Am. Med. Assoc.* 84, 1406-7(1925).—The cases showed beginning sugar excretion levels ranging from 80 to 310 mg. of blood sugar. Coexistence of nephritis with diabetes is apparently the cause of the very high sugar thresholds found. These facts show the importance of blood sugar findings and the insufficiency of urinary sugar exams. in diabetes. L. W. RIGGS

Examination of the spinal fluid. JOHAN LOFTHUS. *Norsk Mag. Laegev.* 85, 705-16(1924).—A review of various reactions used for examg. the spinal fluid in syphilis patients with descriptions and critical evaluations of these reactions. C. H. A. R.

Lipemia. III. Pathological variations in blood fat. H. I. BING AND H. HECKSCHER. *Biochem. Z.* 149, 90-9(1924); cf. C. A. 19, 2232.—Hypolipemia was found in Basedow's disease. Hyperlipemia (fasting values for blood fat greater than 0.25%) was found in acute lung infections, decompensated heart cases, icterus, nephritis and diabetes mellitus. In corpulent individuals with possible endocrine malfunction, the

high blood fat was lowered after administering iodothyrim. In some of the above cases, the hyperlipemia was evident only after a meal. G. E. S.

Variations in the content of normal and pathological urine. A. DE AGUIAR. *Rev. quim. pura aplicada* [3], 1, 136-51 (1924).—Many thousands of samples of urine were analyzed for urea, phosphates, sulfates, chlorides, glucose and albumin during the period 1914-21. The variations in g per liter of each were urea 0.76-50.8, phosphates 0.02-6.62, sulfates 0.13-6.71 and chlorides 0.017-20.36. The max quantities of glucose per liter were 100 g, albumin 30 g. The data were tabulated with reference to analyses and clinical diagnosis. M. H. SOULE.

Experimental obstruction of the jejunum. Effect of sodium chloride introduced directly into the lumen of the intestine below the point of obstruction. R. L. HADEN AND T. G. ORR. *J. Exptl. Med.* 41, 707-18 (1925).—Animals with obstruction of the jejunum were given daily 40 cc  $H_2O$  per kg of body wt. directly into the jejunum below the obstruction, the chem. changes in the blood in all were characteristic of the toxemia of high intestinal obstruction (fall in chlorides, rise in  $CO_2$ -combining power and an increase in the urea and non-protein N).  $H_2O$  alone does not influence the course of the toxemia or have any beneficial effect. One and 2% NaCl solns. prevented a toxemia in uncomplicated cases. Ten % NaCl soln., administered after the onset of toxemia, controlled it in most cases for a long period. HCl had no effect on the course of the toxemia. C. J. WEST.

Liver as a source of bacterial agglutinin. F. S. JONES. *J. Exptl. Med.* 41, 767-78 (1925).—Serum and tissues contg. agglutinin for the hog-cholera bacillus may be dried *in vacuo* over  $H_2SO_4$  without appreciably injuring the antibody. The desiccated material when extd. with appropriate amts. of distd.  $H_2O$  offers a basis for accurate comparison of antibody content. The greatest concn. of agglutinin occurred in the liver, provided the animals injected with small amts. of the antigen were killed within a short period. The serum of those more highly immunized contained the greatest concn. of antibody. A single injection of antigen into a radical of the mesenteric vein resulted in a considerable concn. of agglutinin in the liver. Other expts. indicate that the liver does not act as a reservoir for the antibody. It is also shown that this concn. of agglutinin cannot be ascribed to the blood left within the liver, since the blood serum was relatively poor in antibody. The expts. indicate that the agglutinin was produced within the liver. C. J. WEST.

Surface tension of serum. XIII. Certain physicochemical changes in serum as a result of immunization. P. LECONTE DU NOUV. *J. Exptl. Med.* 41, 779-93 (1925); cf. *C. A.* 19, 1872.—The injection of antigen into an animal determines a gradual change in the blood fluid, which finds expression in 2 physicochem. manifestations that can be readily followed, namely, a decrease in the static value of the surface tension of serum solns. and a special form of crystn. when serum dild. with isotonic NaCl soln. is allowed to evaporate under certain conditions. The change in the blood is at a max. around the 13th day after the 1st antigen injection, and decreases progressively thereafter until it can no longer be observed, which is usually around the 30th day. The change follows the same course, whether a single large injection of antigen is made, or many smaller ones. It begins at the same time in either case; it comes to a max. after the same period and in its subsequent course it is not affected by the reinjection of antigen. The manifestations of the change would appear to be independent of the presence of antigen in the circulation. The mean length of the protein mols. of the immune serum, obtained after the injection of the antigen dealt with, is little if at all different from that of the protein mol. of normal serum. It is possible that this reaction is independent of the antibody formation. C. J. WEST.

## H—PHARMACOLOGY

ALFRED N. RICHARDS

Experimental physiology of the male genitalia. II. Reflexes of the different organs of the male genitalia. ALFRED PEAUTZ AND KONRAD MERDLER. *Arch. Dermatol. Syph.* 148, 98-103 (1925).—IX. Physiology and pharmacology of the spermatic cord *in situ*. *Ibid.* 104-12.—Adrenaline markedly increases the tonus of the spermatic cord in dogs; pilocarpine and physostigmine increase tonus slightly and induce a strong rhythmic stimulation. Ergotamine, pituitrin and quinine, substances active upon the uterus, are inert with the cord. Yohimbine in large doses causes a strong central stimulation; after a latent period moderate amts. increase tonus and induce rhythmic excitation. The cord is paralyzed by papaverine. G. H. S.

Oxidation of benzyl alcohol and benzyl esters in the human organism. I.

SNAPPER, A. GRONHAUM AND S. STURKOP. *Biochem Z* 155, 163-73 (1925).—See C. A. 19, 1598. H. J. C.

The use of iodine in exophthalmic goiter. W. M. BOUTLIBY. *Endocrinology* 8, 727-15 (1925).—The daily administration of I to patients suffering with exophthalmic goiter results in a marked decrease in the basal metabolic rate which reaches its max. about the eighth day at which time the gastro intestinal disorders and nervousness are much improved. The use of I is recommended only as a temporary therapeutic measure. The basal metabolic rate although lowered after its administration remains considerably above normal. W. J. DRYUM, JR.

The use of iodine in exophthalmic goiter. J. MARION REAO. *Endocrinology* 8, 716-56 (1924).—A confirmation of the results obtained by Boutliby (see above abstr.). W. J. DRYUM, JR.

Ether narcosis. L. ZECHNER. *Pharm Monatshefte* 6, 84 6 (1925).—An address. W. O. H.

Spectacular effect of ether anaesthesia on myoclonic encephalitis. ARISTON BANTISTA AND AGERICO B. M. SISON. *J Philippine Islands Med Assoc* 5, 21-3 (1925).—Case report. FRANCES KRASNOW

Observations on the use of novasurol in edema due to heart failure. J. H. CRAWFORD AND J. P. MCINTOSH. *J Clin Invest* 1, 343-54 (1925). See C. A. 19, 1598. LOUIS LEITER

The effect of the ingestion of small amounts of sodium bicarbonate upon the excretion of the "acetone bodies." R. S. HUBBARD AND F. R. WRIGHT. *Ann. Clin. Med* 3, 634-41 (1925).—Increases were found in the excretion of "acetone bodies" at or near the borderline of ketosis when small quantities of  $\text{NaHCO}_3$  were added to the diet. There was both an increased production of "acetone bodies" and a sweeping out of those already produced. JOHN T. MYERS

Mode of action of bismuth in syphilis. C. LEVAMONT AND A. GIRARD. *Compt. rend.* 180, 402-4 (1925); cf. C. A. 18, 1713, 2757, 19, 2088.—Since the publication of the papers above noted, Girard claims to have discovered a method capable of detecting 1 microgram (0.001 of 1 mg.) of Bi in tissues or humors. The method is not described in this paper. Two rabbits, each carrying 2 large syphilitic chancre of the serotum (virus Truffi), were treated with 0.1 g. of "Trepol," an alkali tartrorubinate, per kg. by intramuscular injection. On the 1th day the treponemes had disappeared and the syphilides had diminished in vol. The rabbits were killed on the 4th and 6th day, resp., and their organs analyzed for Bi. The results proved that the content of Bi in the various organs was less in the rabbit killed on the 6th day than in the animal killed on the 4th day; that the kidneys, lungs and spleen contained the most Bi; that the syphilides contained only infinitesimal amounts of Bi. The destruction of the parasite under the action of Bi appears as a lytic process with Bi as a catalyzer. J. W. R.

Blood chemistry in acute histamine intoxication. HIROTORII HASHIMOTO. *J. Pharmacol.* 25, 381-409 (1925).—In shock-like conditions lasting 3-5 hrs. induced by repeated intravenous injection of histamine, there occurred an increase in the non-protein N and the urea N in the blood. There were evidences indicative of impaired renal function and increased protein destruction in the body. There was no consistent change in the chlorides or  $\text{CO}_2$  combining power of the plasma. Blood chemistry characteristic of high intestinal obstruction can be partly, but not completely, reproduced by histamine poisoning, at least not by that of a short duration. C. J. WEST

## I-ZOOLOGY

R. A. GORTNER

Presence of a catalase in the eggs of *Bombyx mori*. I. PICCOLINI. *Arch. Ital. Biol.* 73, 120-5 (1921).—Fecund eggs of *Bombyx mori* decompose  $\text{H}_2\text{O}_2$ . A. T. C.

The influence of certain factors in the development of the flagellum *Prowazekia* (Bodo) edax. H. KAANE. *Bull. soc. chim. Biol* 7, 383-400 (1925).—The factor which dictates the development of a culture of *P. edax* is neither the amt. of nourishment nor the H-ion concn, nor the ratio of the surface of the culture to its vol., but the degree of accumulation of the products of metabolism. A. T. CAMERON

Effect on the blood sugar of fish of various conditions including removal of the principal islets (isletectomy). N. A. MCCORMICK AND J. J. R. MACLEOD. *Proc. Roy. Soc. (London)* 98B, 1-29 (1925).—The sugar content of the blood of salt-water fishes immediately after catching varies considerably among (a) different species, and (b) individuals of the same species. Thus it may range from a trace to 35 mg. per 100 cc. in sculpin (*Myoxocephalus*). Marked hyperglucemia is produced by exposure of fish

to air, e. g., in catching, is apparent within 30 to 45 min., and may give rise to a concn. of 160 mg. within 1 hr., and 200 mg. in 2 or 3 hrs.; it may also be induced by placing fish in a limited vol. of stagnant water, and its rate of development then accelerated by raising the temp. On replacement of fish in frequently changing water, in the sea or an aquarium, at least 2 to 4 days, sometimes longer, are required for a return of the blood sugar to its normal level. The glycogen content of the liver varies with the individual, and usually cannot be correlated with either the normal blood sugar or the degree of hyperglucemia due to asphyxia. Hydrolysis with 0.1 *N* acid produces a marked increase in the reducing power of fresh blood and a smaller increase in the reducing power of its protein-free filtrate. Possibly the asphyxial increase in blood sugar is partly due to hydrolysis of masked or non-reducing carbohydrates in the blood. Sculpin liver has an av. fat content of 26%; this bears no relationship to the glycogen. Blood, taken from either normal or asphyxiated sculpin, oxalated and kept at room temp., does not undergo glycolysis within 10 hrs. Intramuscular injection of adrenaline produces marked hyperglucemia which attains its max. in approx. 2 hrs. Intramuscular injection of insulin has only a slight effect on the blood sugar; removal of the principal islets gives rise to marked hyperglucemia and causes the liver to contain more fat and less glycogen.

JOSEPH S. HEBURN

Influence of certain dyes upon the multiplication of infusoria (*Enchelys*) with special reference to the acridine dyes (acridavine and proflavine). T. B. ROBERTSON. *Australian J. Exptl. Biol. Med. Sci.* 2, 21-43(1925); cf. *C. A.* 19, 1166.—If acridavine be added to hay infusion in any proportion between 1 in 20000 and 1 in 200000 the period of lag of *Enchelys* inoculated into this medium is enormously prolonged. Lower concns. do not prolong lag, but delay subsequent multiplication. Higher concns. are lethal. Previous "acclimatization" of the organisms by exposure from 1 to 5 hrs. to the parent culture fluid, dild. by the addn. of 2 parts of fresh hay infusion, permits division after very prolonged lag, in concns. of acridavine which would otherwise inhibit multiplication for an indefinite period. The subsequent interdivisional periods are similarly prolonged, but, if when they are about to divide in a culture contg. acridavine, the organisms are removed to fresh hay infusion the subsequent interdivisional periods are not prolonged and multiplication proceeds at the normal rate. The younger the parent culture from which the organisms are derived the less the duration of lag in subcultures contg. acridavine. Proflavine acts in a manner similar to acridavine, but is exerted over a narrower range of concns. Scarlet red, phenolphthalein, methylene blue and safranin have no comparable effect upon lag or multiplication of infusoria. Janus green in very narrow concns., about 1 in 10000, caused an indefinite prolongation of the lag. Higher concns. are toxic; lower concns. are without effect.

L. W. RIGGS

Some physiological distinctions between fresh-water and marine organisms. EDW. F. ADOLPH. *Biol. Bull. Marine Biol. Lab.* 48, 327-34(1925).—Marine *Gammarus* will live indefinitely if transferred to sea water dild. with distd. water up to 0.5% (0.005 *M*), or coned by the addn. of salts up to 160% (1.56 *M*, corrected for ionization). Fresh-water *Gammarus* are usually killed by immersion in any soln. of a concn. equiv. to 0.35 *M*. Gradual dildn. or concn. of the medium does not appreciably extend these limits. Existence in the fresh-water medium is accompanied by the possession by all fresh-water organisms of relatively dil. tissue fluids. Apparently it is the integumentary activity which is upset by the increased concns. of the medium and this upset in turn produces rapid changes of a deleterious nature in the compn. of the body fluids. Marine organisms have body fluids which are in complete chem. equil. with their environments.

L. W. RIGGS

Cell size and metabolic activity in Amphibia. H. M. SMITH. *Biol. Bull. Marine Biol. Lab.* 48, 347-76(1925).—Cell size was measured in a no. of species of *Amphibia* by detg. the dimensions and calcg. the area of red blood corpuscles. Metabolic activity was measured by detg. the  $\text{CO}_2$  produced by the animal, and computing the  $\text{CO}_2$  in mg. per g. of body wt. per hr. There is a size variation between corpuscles of the same individual and a variation in the av. size from different individuals of the same species. Smaller animals produce more  $\text{CO}_2$  per unit of wt. than the larger animals. The evidence obtained warrants the conclusion that cell size varies inversely with metabolic activity.

L. W. RIGGS

Respiratory differences along the axis of the sponge *Grantia*. LEBBE II. HYMAN. *Biol. Bull. Marine Biol. Lab.* 48, 379-85(1925).—In the majority of cases apical pieces of the body of the sponge *Grantia* consume  $\text{O}$  and produce  $\text{CO}_2$  at a higher rate per unit wt. than do basal pieces. This result furnishes further evidence in favor of the axial gradient conception.

L. W. RIGGS

Relations of carbon dioxide to the spontaneous movements in the larvae of *Op-*

sansus tau. H. C. TRACY. *Biol. Bull. Marine Biol. Lab.* 48, 408-31(1925).—Newly hatched and free swimming larvae of toad fish were subjected to different concns. of  $\text{CO}_2$  produced by addns. of different percentages of 0.05 N HCl to sea water. Increased concn. of  $\text{CO}_2$  is followed by an increase in the endogenous (spontaneous) body movements in both stages; in newly hatched larvae the reaction to  $\text{CO}_2$  is less intense but of greater duration (av. 25 min.) than in the free swimming larvae (av. 10 min.). On return of larvae to normal sea water from the higher concn. of  $\text{CO}_2$ , the frequency of body movements is depressed below normal; the depression is less in the newly hatched larvae than in the free swimmer and recovery is slower. In the lower ranges of  $\text{CO}_2$  concn. the body movements in both stages and the rate of respiratory movement in free swimmers vary with increase in  $\text{CO}_2$ . On return to normal sea water the body movements for all concns. of  $\text{CO}_2$  remain depressed for a time; the rate of respiratory movement is below normal for the lower concns. but is increased above the normal on return from higher concns. Toad fish larvae are much more resistant to asphyxial conditions than are adults. It is suggested that the migration of fishes in a H-ion gradient is probably conditioned by the effect of acid substances on the endogenous body movements. It is suggested that stimulation by variation in the concn. level of metabolites produced inside the body may be the source of endogenous (spontaneous) movements. L. W. RIGGS

Toxicity of oxygen for protozoa in vivo and in vitro: animals defaunated without injury. L. R. CLEVELAND. *Biol. Bull. Marine Biol. Lab.* 48, 455-68(1925).—The toxicity of O under various pressures for 4 generations of termites was detd. At a pressure of 3.5 atm. the protozoa were all killed in 30 to 40 min. while the termites themselves survived for 45 hrs. This makes it possible to remove all protozoa from termites without injury to the host. By similar methods O was found to be 135 times as toxic to flagellates and 26 times as toxic to ciliates, each living in cockroaches, as it is to the insects themselves. Earthworms when oxygenated lose their ciliates and are uninjured by the process. Frogs harbor many protozoa. All intestinal protozoa may be removed by oxygenation without injury to the frogs. Similar results occurred with gold fish and with salamanders. Trichomonas cannot be removed from rat or man by oxygenation at 3.5 atm. Perhaps trichomonas may be removed by the administration of O in a different way. L. W. RIGGS

Feeding habit of termite castes and its relation to their intestinal flagellates. L. R. CLEVELAND. *Biol. Bull. Marine Biol. Lab.* 48, 295-305(1925).—More than 100 genera and approx. 1200 species of termites are known and each species is usually composed of 5 castes with male and female individuals in each. Three of these castes are responsible for the reproduction of individuals like themselves and of 2 other castes, workers and soldiers, resp. which do not exercise the reproductive function. At every stage in the life cycle of any caste when wood is eaten protozoa are present. When wood is not eaten or obtained in some way, protozoa are never present. A caste which cannot eat wood, that is, which does not harbor protozoa, cannot live by itself, but is dependent upon the wood-eating members of the colony for support. This is the fact with castes of the second form, third form and soldiers. The latter, however, can digest partially digested woody material, which has passed through the alimentary canal of the xylophagous members of the colony, before they receive it. The second and third forms feed exclusively on salivary secretions and therefore must subsist entirely on predigested food. Effects of oxygenation and starvation on the symbiosis between the termite *Termopsis* and its intestinal flagellates. *Ibid* 309-26.—*Termopsis* termites were freed from wood particles and were placed in Petri dishes in a chamber kept at the proper humidity where they were subjected to starvation. Thus the termites lose their various protozoa from day to day up to the 15th day when most of the protozoa are dead. A few live 3 to 4 weeks or almost as long as the termites themselves. In fairly pure O the protozoa were all removed within 72 hrs. and certain species within 24 hrs. By starvation and by oxygenation it is possible to shift the protozoa almost at will, and leave the termites with the particular species of protozoan desired. This was done and the results as regards the symbiotic relationship between termites and their intestinal protozoa were found to be in accord with those obtained by the incubation method. (Cf. C. A. 18, 2389.) L. W. RIGGS

Action of external factors upon Infusoria. The conjugation of *Glaucoma scintillans* determined by modification of the proportions of the constituents of a chemically definite medium. EDOUARD CHATTON AND (MME.) CHATTON. *Compt. rend.* 180, 1137-9(1925).—The medium used consisted of  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ , 2 g.,  $\text{K}_2\text{HPO}_4$ , 0.8,  $\text{NaClO}_3$ , glucose 0.5,  $\text{H}_2\text{O}$  1000. In a "pure-mixt" culture *Glaucoma scintillans*-*B. fluorescens* the bacteria develop first but by the 5th day are totally exhausted by the growth of the Infusoria which have reached a density of 12 to 15 thousand per cc. The development

of the Infusoria is now arrested, as much by intoxication as by starvation, since by addn. of bacteria but little further development of the Infusoria results. This phase is called the cultural crisis. For conjugation to occur the concn. of the salts in the medium must be reduced to 0.6, 0.25 and 0.1 g., resp. per 1000, the glucose remaining at 0.5. Increasing the glucose with the salts remaining at their original concn. was not followed by conjugation. L. W. RIGGS

Function of the foodstuffs dissolved in the water in the metabolism of aquatic animals. V. Effect of stimulation of the intestinal wall by indigestible substances upon the assimilation of dissolved foodstuffs. JAROSLAV KRIZENECKÝ AND JAN PODHRADSKÝ. *Arch. ges. Physiol.* (Pflüger's) 207, 508-14 (1925), cf. C. A. 18, 3209.—*Rana* tadpoles were kept in solns. contg. either peptone and sucrose or "Buiklein". The animals in each of these nutritional fluids were divided into two groups, and to the medium contg. one group of each series powdered cellulose was added. Detns. of the rate of growth, and of both live wt. and dry wt. showed that the mere filling of the intestinal tract exerted no effect upon assimilation. G. H. S.

## 12—FOODS

W. D. BIGELOW AND A. E. STEVENSON

The destruction of organic matter. M. WAGENAAR. *Pharm. Weekblad* 62, 557-63 (1925).—For the purpose of testing for heavy metals the org. matter of food products may be destroyed by heating with a mixt. of  $H_2SO_4$ ,  $HNO_3$ , and  $K_2SO_4$ . A. W. DOX

Effect of storage on the composition of a noodle and judging the degree of decomposition of the lipoids. RAYMOND HEATWIG. *J. Assoc. Official Agr. Chem.* 8, 435-9 (1925), cf. Buchanan, C. A. 18, 2394.—Analysis of a sample of noodles shortly after manu. and 22 months later by all the A. O. A. C. methods of noodle analysis indicate the compn. of the solids kept under fairly dry conditions changes somewhat with respect to the lipoids but remains practically const. as far as results of the other methods are concerned, the methods for fat (by acid hydrolysis) and  $H_2O$ -sol. protein-N precipitable by 40% EtOH det. those components that remain practically unaltered during av. storage conditions, the relations between lipoid  $P_2O_5$ , lipoids, fat (by acid hydrolysis), and alk. precipitable N are not changed sufficiently during storage to interfere with differentiating between whole-egg and com.-yolk noodles; the ratio of lipoids to fat indicates the degree of decompn. of the lipoids and lipoid  $P_2O_5$ , being above 1 (about 1.1-1.2) in fresh noodles and gradually falling to below 1 on storage. It indicates the degree of dependability of the estd. egg solids by the formula method involving the lipoid  $P_2O_5$ . A. PAPINEAU-COUTURE

Determination of the salt content of clams. D. B. DILL. *J. Assoc. Official Agr. Chem.* 8, 447-8, 450 (1925).—Comparative Cl detns. after ashing with and without addn. of  $Na_2CO_3$  showed losses of 13-42% of the Cl in the latter case. A. P.-C.

Rapid routine method for total solids determination in eggs. RAYMOND HEATWIG AND L. H. BAILEY. *J. Assoc. Official Agr. Chem.* 8, 451-4 (1925).—A vacuum method (to be published), consisting essentially in drying at 98-100° under not more than 25 mm. of Hg (abs.) is suitable as a conventional umpire method, but requires rather elaborate equipment and considerable time, and is not economical for general use. Results concurring with those of the above vacuum method are obtained by drying at atm. pressure, at 112-7° in Al dishes, 55 mm. in diam., 15 mm. high, provided with slip in inverted covers fitting tightly on the inside. For dried eggs dry approx. 2 g. for 1 hr. For liquid egg dry approx. 5 g. on the steam bath for 30 min., and then at 112-7° for 3 hrs. The results are not affected by slight variations in time and temp. A. P.-C.

The indole content of canned crustacea. D. B. DILL AND P. B. CLARK. *J. Assoc. Official Agr. Chem.* 8, 449, 451 (1925).—Examn. for indole of freshly cooked meat, meat immediately after canning and 6 months after canning of Dungeness crab (*Cancer magister*), Puget Sound shrimp (species unknown) and California spiny lobster (*Panulirus productus*) gave distinctly positive tests in most cases. Further examn. of different portions of vivisectioned spiny lobsters indicated that indole is not a normal constituent of the flesh; its presence in canned crustacean meat may be due to its escape from the alimentary tract into the flesh during cooking. A. PAPINEAU-COUTURE

A study of methods for making protein tests on wheat. D. A. COLEMAN, H. C. FELLOWS AND H. B. DIXON. *Cereal Chem.* 2, 132-64 (1925).—No uniform method is used by the different labs. Three general types of methods, with various modifications, were used by 38 labs. The results showed a max. difference of 3.15%. It is suggested that a referee lab. should be established to settle disputes of any nature, arising out of

the practice of making protein tests. Details of the methods are well discussed and certain recommendations are made.

**Preserved olives as food.** THEO. STATHOPOULOS. *Chem. Umschau* 32, 73-5 (1925).—Each type and grade of olives is treated in a different way for purposes of preservation. The following table shows the analytical data of a no. of Greek varieties.

	Black from Attica	Green from Attica	Black from Calamata	Black from Salona	Black from Volo
% Meat	68.62	77.53	70.75	67.80	69.50
% Kernel	22.22	16.27	23.00	24.25	23.90
% Hulls	9.14	6.20	5.25	7.95	6.60
Av. wt. of 10 olives in g.	36	51.6	50	42	45
Compn. of Meat:					
H <sub>2</sub> O	41.02	67.96	51.81	49.42	31.50
Oil	23.31	15.26	27.28	24.22	30.09
Nitrogen	0.63	0.25	0.23	0.29	0.25
Extractives	(21.90)	(6.33)	(17.54)	(19.35)	(21.89)
Carbohydrates	10.45	3.59	6.34	5.02	8.80
Cellulose	3.73	1.05	2.90	5.42	3.13
H <sub>2</sub> O-sol. ext.	7.72	1.69	8.21	8.01	12.96
Ash	10.14	10.20	3.14	6.72	9.31
	100.00	100.00	100.00	100.00	100.00

Ash:					
NaCl	10.08	9.92	0.20	3.53	1.82
P <sub>2</sub> O <sub>5</sub>	0.0656	0.011	0.078	0.00202	0.0564
Calories	4651	1800	4801	3737	4889

P. ESCHER

**The individuality of glutenin.** M. J. BLISH. *Cereal Chem.* 2, 127-31 (1925).—Wheat flour glutenin is a chem. individual which cannot be fractionated into 2 parts as claimed by Halton. B.'s expts. show that Halton's conclusions that each flour contains 2 glutenin "fractions" of different chem. configuration and that flour strength depends on which of these "fractions" predominates, is founded upon insufficient and mistaken evidence. It is shown that racemization of glutenin (even though slight) gives rise to a second "fraction" which has a different isolec. point from that of natural glutenin, and it also results in other products which can be pptd. only by use of heavy reagents such as phosphotungstic acid. B. believes that Halton's "fractions" were obtained from a glutenin which had been slightly racemized before he fractionated it.

RUTH BUCHANAN

**Triers for sampling flour.** H. E. ROETHE. *J. Assoc. Official Agr. Chem.* 8, 424-35 (1925).—The H<sub>2</sub>O content of sacked flour near the outer surface at times differs materially from that at the center. A correctly designed trier should remove proportionate quantities of flour from the various zones, the quantity taken from each zone being detd. by the % vol. of the entire sack represented in such zone. Neither the 30 in. tubular trier nor the Jabez Burns & Sons No. 4 trier fulfills this condition. Five different types of triers which fulfill the condition to varying degrees of approximation are submitted for consideration.

A. PAPINEAU-COUTURE

**"Neutralizing value" of monocalcium phosphate.** L. H. BAILEY. *J. Assoc. Official Agr. Chem.* 8, 444-7 (1925).—Titration with standard alkali does not give a true measure of the NaHCO<sub>3</sub> which can be neutralized by CaH<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub> in baking powders and self-rising flours. Mixts. of phosphate with decreasing proportions of NaHCO<sub>3</sub> were analyzed for residual CO<sub>2</sub> (A. O. A. C. tentative gasometric method, C. A. 17, 2621) and for p<sub>H</sub> (1 g. boiled with 100 cc. of H<sub>2</sub>O till free from CO<sub>2</sub>, and then cooled). With p<sub>H</sub> of 7.0 or less, there is no residual CO<sub>2</sub>, showing that the correct neutralizing value is that which gives p<sub>H</sub> = 7.0. B. suggests this for detg. the true "neutralizing value," and checking by detg. residual CO<sub>2</sub>.

A. PAPINEAU-COUTURE

**Variations in the percentage of butter fat in milk.** A study based on New Zealand C. O. R. data. W. N. PARON. *New Zealand J. Agr.* 29, 191-7, 305-11 (1924); 30, 77 (1925).—The factors influencing the butter-fat content of milk are the breed, time of commencement of lactation during the year, length of period of gestation, nature of season, and condition and feeding of the cows. Numerous tables of results are given.

K. D. JACON

Some little-studied constituents of milk. L. B. BLEYER AND O. KALLMANN. *Biochem. Z.* 153, 459-86(1924).—A study is made of the non protein nitrogenous substances, the water-sol. colored substances, and some inorg. salts of milk. After removal of fat by use of a centrifuge, the effect of the addn. of varying amts. of acid and alkali upon the coagulation temp. was observed. The N distribution as the milk is fractionated is detd. In addn., analyses for urea N, amino N,  $\text{NH}_3$  N, creatine, creatinine and uric acid are made. No new substances are reported.

W. D. LANGLEY

Membrane of the fat globule of milk. K. HATTORI. *J. Pharm. Soc. Japan* No. 516, 123-70(1925).—If a drop of milk is examd. in a quartz chamber with the ultramicroscope, fat globules and granular particles are observed, the latter showing Brownian movement. When milk is frozen and examd. at room temp. the shape of the fat globules appears the same, except now the globules show not only a well marked membrane but also some granules within them due probably to sepn. of some higher melting fats; this phenomenon is irreversible. If a drop of milk is air-dried, and extd. with  $\text{Et}_2\text{O}$ , acetone, or  $\text{CHCl}_3$ , the globular membrane and some of the granules are left intact, showing a spotty appearance, suggesting that there is in the membrane and globules some substance insol. in fat-solvents, which when left in  $\text{H}_2\text{O}$  loses its globular appearance. When 1 part of milk is treated with 9 parts  $\text{H}_2\text{O}$  satd. with  $\text{CHCl}_3$  (20°), and left over 48-72 hrs., the liquid seps. into 2 layers, the upper contg. no globules, but granules showing Brownian movement, the lower contg. the globules, which are now 2-4 times the original size. Calcn. shows that under this condition the globules absorb 84.77%  $\text{CHCl}_3$  from the liquid. By repeating 4 times with this  $\text{CHCl}_3$ - $\text{H}_2\text{O}$  treatment, and extg. the fat from the globules with  $\text{Et}_2\text{O}$ , H. obtained a white powder which corresponds to the membrane of the fat globules; he gives it the name *haptein*. Haptein contains 1.954% ash, 12.056% N, 2.58% S, the ash consisting mainly of Ca and  $\text{P}_2\text{O}_5$ . The ash content is not decreased after dialysis, except in dialysis in HCl (ash content decreases 1.2% from original 3.1%). It is not hygroscopic, has no taste, no odor, is insol. in  $\text{H}_2\text{O}$ , but produces a suspensoid when shaken; not sol. in dil. acid, alkali, strong acid, but sol. in a strong alkali. From alk. solu. it can be reprecipitated with an acid. It is insol. in hot or cold absolute or 50% alc., even after treating with an acid; insol. in dil. salt solns.; it swells in  $\text{H}_2\text{O}$  or alk. soln.; no reducing substance is obtained by an acid hydrolysis (5% HCl); it gives biuret, xanthoproteic, Millon, Adamkiewicz, Reiehl reactions but no furfural reaction, nor Liebermann, contg. therefore no tryptophan. 100 parts of N are distributed as follows: 9.987 amino N, 3.484 amines, 5.336 cystine, 12.788 arginine, 5.436 histidine, 6.113 lysine, 55.131 mono amino N, 1.610 non-amino N. With the exception of keratin, haptein has the highest cystine content of all the proteins. Like keratin, it is low in lysine. These analyses show that haptein is a protein, unlike any other proteins present in milk. It contains no vitamins. Various considerations involved in the formation of emulsions are given.

S. T.

Milk in bread. A. F. GERHARD. *Northwestern Miller* 142, 829(1925).—A detailed description is given of the use of fresh, homogenized, pasteurized, powd., evapd., condensed and skimmed milk and buttermilk in bread. The distinction between the milks is defined. Adulterants and preservatives are discussed. Comparative analytical results and comparative costs of the use of these various milks are mentioned. It is in reality cheaper to make milk bread than water bread.

RUTH BUCHANAN

The role of rennet and its mode of action in the manufacture of heated-curd cheeses (Gruyère and Emmenthal). G. GUTTONNEAU. *Compt. rend.* 180, 1536-8 (1925).—By increasing the acidity of the milk with 0.1 g. of lactic acid per l., by means of an addn. of strongly acidified whey sterilized and filtered, the conditions of action of the rennet are but slightly improved. Increasing the lactic leavens from 2 to 10 per 1000 fails to produce the desired results. The addn. to the milk in the kettle of 0.125 to 0.250 g. of  $\text{CaCl}_2$  per l., causes rapid coagulation and the production of cavities characteristic of this variety of cheese. A combination of acidification of the milk and addn. of  $\text{CaCl}_2$  gives the best results.

L. W. RIGGS

Why determine shell content of cacao powder? O. P. A. H. SCHAAP. *Pharm. Weekblad* 62, 609-13(1925).—The cacao butter content is considered a more logical criterion of purity than the shell content.

A. W. DOX

Sugar-beet pulp and slices. R. N. DOWLING. *J. Ministry Agr.* 31, 750-7(1924).—Expts. on cows showed that the dried pulp from the sugar beets served as a satisfactory food in conjunction with mangolds from the standpoint of the quantity and quality of the milk production.

H. J. DEUEL, JR.

Report on maple products. H. M. LANCASTER. *J. Assoc. Official Agr. Chem.* 8, 372-4(1925).—The method of detg. the Canadian Pb no. (pptn. with basic Pb acetate and weighing the ppt. directly) is described. Results of collaborative work indicate that

the  $pH$  of the basic Pb acetate soln. may vary between 7.3 and 7.7, that high  $pH$  tends to give slightly higher Pb no., that the importance of slight differences in the reagent has been somewhat exaggerated, that the washing of the ppt. is the step requiring standardizing, and that the technic, as it stands, is sufficiently accurate to supply figures that are a valuable index of the genuineness of maple products. A. P.-C.

**Honey**—detection of artificial invert sugar. WILLIAM SEAMAN. *J. Assoc. Official Agr. Chem.* 8, 364-71(1925); cf. Sherwood, *C. A.* 16, 2369; 18, 2391.—Further collaborative work has on the whole confirmed previous conclusions. The resorcinol (Bryan's modification of Fiehe's) test and the aniline chloride (Feder) test, when positive, are conclusive of the presence of com. invert sugar, unless the honey was stored for some length of time after having been heated above 160° F. When negative, these tests are not conclusive of the absence of com. invert sugar. A. PAPINEAU-COUTURE

**Method for the determination of starch in the presence of interfering polysaccharides.** M. R. COE. *J. Assoc. Official Agr. Chem.* 8, 358(1925); cf. *C. A.* 18, 2395.—In order to obtain a sample free from lumps when the material is gelatinized, after washing with Et<sub>2</sub>O, 35% EtOH, and again with Et<sub>2</sub>O, and drying to remove EtOH, transfer as much of the dry material as possible to a glass mortar, pulverize all lumps, transfer both paper and sample to a 500-cc. volumetric flask, add 20-30 cc. H<sub>2</sub>O, shaking vigorously till the sample is completely wetted, let stand a few min., add 100 cc. of actively boiling H<sub>2</sub>O with occasional shaking to prevent local heating. If more than 20-30 cc. cold water is required, calc. the quantity of hot H<sub>2</sub>O so that the total vol. including 40 cc. of malt soln. will not exceed 200 cc. A. PAPINEAU-COUTURE

**A study of the principal changes which take place in the making of silage.** W. H. PETERSON, E. G. HASTINGS AND E. B. FRED. *Univ. Wisc. Agr. Expt. Sta., Res. Bull.* 61, 32 pp.(1925).—The expts. were conducted with a specially built silo, 10' X 30', filled with high-grade corn. O disappeared from the silo gases in 5 hrs. after filling. CO<sub>2</sub> increased rapidly for 48 hrs. when it amounted to 65% of the gases. No H nor hydrocarbon gases were present. In 15 days the temp. rose 7° near the bottom and 20° near the top. It then fell gradually but at the end of 70 days was still above normal. During the first 48 hrs. the amt. of EtOH, AcOH and lactic acid and no. of bacteria increased rapidly. Of the bacteria, the lactic acid formers and pentose-fermenters were present in greatest nos. Yeast cells diminished in no. rapidly after the first day. Ten % of the dry matter, 25% of the pentosans and 25% of the starch had disappeared at the end of 4 mos. Sterilized corn forage inoculated with *L. pentoceticus* produced silage similar in compn. to normal silage. A bibliography of 30 citations is appended. A. L. M.

**Silani:** a new cover and forage crop from the Philippines. P. J. WESTER. *Trop. Agr. (Ceylon)* 64, 32-4(1925).—*Vigna marina*, Merr., commonly called silani, contains H<sub>2</sub>O 65.77, protein 3.17, carbohydrates 24.25, fat 0.83, fiber 4.04 and ash 1.84%. Its nutritive value is 29.3 as compared with 11 for cowpeas. A. L. MEHRING

**Partial substitution of other fodder for hay.** J. C. DE RUYTER DE WILDT AND E. BROUWER. *Verslag Land. Onderzoek. Rijkslandbouwschool.* 1924, No. 29, 61-63; *Chimie et industrie* 13, 833(1925).—Substitution of a mixt. of wheat bran 7, corn meal 3, dried pea leaves 7, and oat straw 11, for 1/3 of the hay ration had no effect on the quantity or quality of the milk, nor on the wt. of the animals. A. P.-C.

**Poisoning of cattle by sweet clover hay.** ALVIN BROERMAN. *J. Am. Vet. Med. Assoc.* 67, 367-72(1925).—Report of cases showing on post mortem exam. large hemorrhagic areas in various parts of the body. The nature of the toxic substance has not been detd. FRANCES KRASNOW

**Effect of temperature and diminished pressure in the determination of moisture in feeding stuffs.** L. E. BOPSY, A. L. FLENNER AND O. H. REINMUTH. *J. Assoc. Official Agr. Chem.* 8, 354-7(1925).—Reducing the pressure below 18 in. of Hg (abs.) in drying feeds at 98.5° has little or no practical effect on results. After equil. has been attained at a pressure of 18 in. of Hg, further heating removes only a small quantity of moisture. Drying at 100° at atm. pressure is not a practical method. Heating at 110-25° for 1-4 hrs. gave very unsatisfactory results. A. P.-C.

**Analysis of fluosilicate and fluoride mixtures in organic substances** (NOETZEL) 7.

FRANZEN, HANS: *Margarine* (in German). Leipzig: Otto Spamer. 100 pp. Unbound, G. M. 10; bound G. M. 12. Reviewed in *Chem. Age* (London) 12, 553 (1925).

**Sterilizing milk.** N. J. NIELSEN. U. S. 1,541,994, June 16. See Brit. 227,046 (*C. A.* 19, 2094).

Starch-free bran. J. TAKAMINE, JR. U. S. 1,543,458, June 23. Bran is cooked until the starch cells are opened, mixed with diastatic enzyme to convert the starch into dextrin and sugars, and washed to remove these conversion products. The bran residue is suitable for use as a laxative food ingredient.

Apparatus for preparing powdered cocoa. P. G. HOLLSTEIN. U. S. 1,542,884, June 23.

### 13—GENERAL INDUSTRIAL CHEMISTRY

HARLAN S. MINER

Crushing and grinding. III. S. G. URE. *Chemistry & Industry* 44, 551-9 (1925); cf. C. A. 19, 2004.—A very complete description is given of ball and tube mills, machines with shearing action, and ring roller mills. L. A. PRIDGON

Technology of leaching and extraction. A. W. ALLEN. *Chem. Met. Eng.* 32, 561-5 (1925). E. H.

The drying process. F. C. BECKER, C. JANHOLM AND P. E. RAASCHOF. *Dunsmuir's Notiser* No. 9A, 33 pp (1925).—A study of the evapn. process under tech. conditions. An expil app to investigate the interdependence of the rate of evapn., and the velocity of air, the drying temp., and the quantity of moisture in the drying air is described and illustrated. A formula is given which, taking into account the velocity of air, permits calcn. of the rate of evapn. with deviations varying from  $-1\frac{1}{2}\%$  to  $+28\%$ . To illustrate how the new formula may be used, partly for calcn. of a drying plant and partly for dimensioning a drying plant, three examples are figured out. Dalton's formula, into which the velocity of air does not enter, shows wider deviations between calcd. and expil. values. W. H. BOYNTON

The new development of the Krause drying process. OETKEN AND HATSER. *Z. angew. Chem.* 38, 341-6 (1925).—The liquid to be evapd. is introduced into the heating chamber as a spray, suitable settling chambers being provided for the dry powdered product. It is particularly applicable to evapn. of solns. of substances which are sensitive to heat, such as urea, enzymes, drugs, easily hydrolyzed inorg. salts, etc. A complete description of the process and app. is given (with 2 diagrams). W. B. P.

Dielectric-strength-thickness relation in fibrous insulation. F. M. CLARK AND V. M. MONTSINGER. *Gen. Elec. Rev.* 28, 286 (1925). C. G. F.

Industrial metal poisoning. GEORG WOLFF. *Chem.-Ztg.* 49, 411-2 (1925); cf. C. A. 19, 2247.—A general article on occupational poisoning and other hazards in the Fe, Cu, Zn, Hg, noble-metal, Cr, As and P industries. HARRIET W. GIBSON

A case of poisoning by nitrobenzene. R. FROSSARD. *J. pharm. chim.* [8] 1, 478-80 (1925).—A boy, age 14, having swallowed the equiv. of a teaspoonful of  $\text{PhNO}_2$ , some of which was vomited, recovered after 20 days. The severe symptoms and the treatment (mainly washing out the stomach) are described. S. WALDBOTT

Some cases of phosgene poisoning. GEORGE BOX. *Medicinsk Revue* 42, 1-23 (1925).—The course and treating of 12 cases of  $\text{COCl}_2$  poisoning, which occurred during a fire, are described in detail. C. H. A. ROBAK

Use of carbon monoxide gas masks in mines. S. H. KATZ, G. S. MCCABE AND A. L. BAKER. *Carnegie Inst. Technology. Coal Mining Investigations Bull.* 14, 72 pp. (1924).—An exhaustive study of the use of the Universal type gas masks in mines leads to the conclusion that the All-Service masks may be safely used as long as a flame can be maintained in a safety lamp. The latter requires  $16\frac{2}{3}\%$   $\text{O}_2$ , whereas man is not endangered until the  $\text{O}_2$  is reduced to 12-13%. The use of this type of mask has resulted in the saving of considerable property and several lives. W. H. BOYNTON

Annual Reports of the Society of Chemical Industry on the Progress of Applied Chemistry. Vol. IX, 1924. London: Society of Chemical Industry. 7s. 6d. to members of the Society, 12s. 6d. to non members. Reviewed in *Intern. Sugar J.* 27, 273 (1925).

Vaporizing water and humidifying air with the vapor. R. W. HARDIE. U. S. 1,542,696, June 16.

Electric insulating material. WESTERN ELECTRIC, NORSE A.-S. Norw. 40,995, March 2, 1925. An elec. insulating material of high resistance and low electrostatic capacity, particularly suited for long use in sea-water, and of nearly the same quality as gutta-percha, is manufactured from rubber approx. free from water-sol. substances and a water-insol. filler approx. free from water-sol. impurities.

## 14—WATER, SEWAGE AND SANITATION

EDWARD BARTOW AND G. C. BAKER

The presence of iodates in the waters of northern Santa Fe. A positive Trommsdorff reaction caused by iodates in absence of nitrites. C. F. HICKETHIER and ALBERTO JACOBUCCI. *Rev. facultad cienc. quim.* 3, 93-105(1925) M. J.

Analysis of the water of a spring near Soultz-sous-Forêts (Alsace). A SARTORY and R. SARTORY. *Strasbourg médical* July 5, 1924. *J. pharm. Alsace Lorraine*, 51, 235-7(1924).—Bacteriol. and chem. exams. show the water to be pure and of low mineral content. S. WALDBOTT

Development of the Charlotte (N. C.) water works. W. E. VEST. *J. Am. Water Works Assoc.* 13, 655-60(1925) E. H.

Water-works practice in Quebec. T. J. LANFRENIERE. *J. Am. Water Works Assoc.* 13, 613-8(1925).—A historical review E. H.

The influence of  $p_H$  on the clarification of water. E. E. J. BACHMANN. *Rev. facultad cienc. quim.* 3, 107-15(1925).—The entire  $Al(OH)_3$  of water can be pptd. by  $NaOH$  or  $NaHCO_3$  at  $p_H$  10. In an acid medium a higher acidity was required for the clarification. The fairly constant  $p_H$  7.1-7.2 of the Rio de la Plata water is reduced to 5.56-6.96 by the alum treatment of the municipal water supply of Buenos Aires and rises to 6.8-7.0 after filtration. Addn. of  $Ca(OH)_2$  may raise the  $p_H$  to 7.2-7.4 or even to 7.5 if the flow of water is very slow. It always decreases after filtration. The  $p_H$  of the waters of Argentina varies between 6.8 and 8.0. MARY JACOBSON

Experiences in connection with the chemical control of a water-purification plant using chlorine gas. FRITZ EGGER. *Chem.-Ztg.* 49, 397-8(1925).—Chem. control methods used in the filtration plant of Stuttgart are discussed. The benzidine Cl test is used for both qual. and quant. colorimetric detns. As the standard benzidine solns. do not keep, E. uses  $CuSO_4$  (5 aq.) solns. of different strength. As a check the volumetric method for Cl with a 0.02 N thiosulfate soln. is used. The use of o-toluidine for the identification of free Cl was not satisfactory. J. C. JURRIJENS

Over-chlorination for taste control. W. B. BUSHNELL. *J. Am. Water Works Assoc.* 13, 653-4(1925).—See C. A. 18, 3241. E. J. C.

Volumetric determination of ammonia in water. J. GOLSE. *Bull. soc. pharm. Bordeaux* 63, 10-4(1925).—The detn. is based on the following reactions.  $2NH_3 + 3NaBrO = 3NaBr + 3H_2O + N_2$ ,  $HBrO + 2HI = HBr + H_2O + I_2$ ,  $2Na_2S_2O_3 + 5H_2O + I_2 = 10H_2O + Na_2S_2O_4 + 2NaI$ . One cc. of the  $Na_2S_2O_3$  soln. corresponds to 0.1 mg. of  $NH_3$ . The  $NaBrO$  soln. is prepd. by mixing 1 cc. of Br and 10 cc. of  $NaOH$  soln. (30%) with sufficient  $H_2O$  to make 500 cc. To make the test, 500 cc. of the sample of  $H_2O$  is made alk. with  $NaOH$  or  $Na_2CO_3$  and distd. in a suitable app. two 100-cc. fractions being collected. Into each of two 250-cc. flasks provided with ground-glass stoppers introduce 10 cc. of the  $NaBrO$  soln. Add 100 cc. of  $NH_3$ -free  $H_2O$  to one of the flasks and 100 cc. of the distillate to the other. Shake the 2 flasks simultaneously for 1 min. and then immerse them in a bath of cold  $H_2O$  for 10 min. Pour 5 cc. of a 20% soln. of KI into each flask, add 5 cc. of a 10% soln. of  $AcOH$  and 1 cc. of starch indicator. Titrate the I liberated with the  $Na_2S_2O_3$  soln. A. G. DUMÉZ

Report on waters, brine and salt. (Determination of hydrogen sulfide in water.) C. H. BADGER. *J. Assoc. Official Agr. Chem.* 8, 329-33(1925).—Solns. contg. about 100 mg. per l.  $H_2S$  cannot be agitated in the slightest degree without causing loss of  $H_2S$ . Addn. of substantial quantities of org. matter,  $NaHCO_3$ ,  $NaCl$ ,  $Na_2SO_4$  or  $MgSO_4$  to  $H_2S$  solns. with  $p_H$  of 5.0-2.6 does not affect the results. With a  $p_H$  of about 8.9  $NaHCO_3$  gives high results; samples contg. added  $NaHCO_3$  which have been subsequently made acid to phenolphthalein give satisfactory results; reducing the  $p_H$  to 1.5 by addn. of 1:1  $HCl$  with or without addn. of org. matter,  $NaCl$ ,  $Na_2SO_4$  or  $MgSO_4$  gives results about 5% low. B. recommends dropping the present A. O. A. C. method and adopting a technique (described in detail) consisting essentially in neutralizing to phenolphthalein with 0.05 N  $HCl$  or  $NaOH$ , titrating with 0.02 N or 0.01 N I in presence of starch indicator, and then repeating the detn. on a fresh portion to which is immediately added the required quantity of  $HCl$  or  $NaOH$ , and 0.5 cc. less than the calcd. quantity of I, and finishing the titration immediately. A. P. C.

The anaerobic destruction of organic materials in sewage sludge by bacteria. BACH AND SIERP. *Centr. Bakt. Parasitenk.* 2 Abt., 62, 24-76(1924).—Many org. substances were separately inoculated with sewage sludge, and after incubation analyses made of the culture mediums. Among the substances were raw and cooked beef, raw and cooked potato, egg white, glucose, fresh and dried carrots and feces. Detailed data

are given as to the quantity and compn. of gas formed, and of org and mineral matter remaining. JOHN T. MYERS

Practical disinfection. LOUIS GERSHENFELD. *Am. J. Pharm.* 97, 307-24(1925).—A popular lecture. W. G. GAESSLER

### Nessler's reagent without KI (WINKLER) 7.

Apparatus for filtering and softening water. J. E. CAPS. U. S. 1,541,921, June 16.

Apparatus for chemical purification of water. I. B. TANNER. U. S. 1,542,186-7, June 16

Apparatus for generating fumigating gas from hydrocyanic acid. K. F. COOPER. U. S. 1,541,793, June 16.

Garbage disposal. C. R. FOX and W. S. DAVIS. U. S. 1,543,154, June 23. Garbage is mechanically reduced to finely subdivided condition and then is passed through a sewage putrefaction system.

## 15—SOILS, FERTILIZERS AND AGRICULTURAL POISONS

J. J. SKINNER

Comparative experiments on the efficacy of nitric nitrogen used alone and of ammoniacal nitrogen in the presence of partial sterilizers of the soil. G. RIVIERE AND G. PICHARD. *Compt. rend.* 180, 1034-6(1925).—Used alone  $(\text{NH}_4)_2\text{SO}_4$  gave lower increases in yield of spring oats than an equiv. amt. of  $\text{NaNO}_3$ ; but when applied in conjunction with an antiseptic salt, such as  $\text{Na}_2\text{AsO}_4$  or  $\text{CaSO}_4$ , which favors nitrification by destroying protozoa inimical to nitrifying organisms,  $(\text{NH}_4)_2\text{SO}_4$  yielded as high or greater increases than  $\text{NaNO}_3$ . P. R. DAWSON

Effect of cropping upon the active potash of the soil. G. S. FRAPS. *Texas Agr. Expt. Sta., Bull.* 325, 15 pp (1924).—The active K, which is the K dissolved by 0.2 N  $\text{HNO}_3$ , is decreased when crops are grown upon the soil. The soils studied were cropped in pot expts. with addns. of dicalcium phosphate and  $\text{NH}_4\text{NO}_3$ . The amt. of active K lost from the soil in 409 expts. averaged 40.9% of the K removed by the crops. As successive extns. of the soil with the solvent remove active K, and the soil also has a fixing power for K, the active K lost by cropping must be less than the K removed by cropping. The correlation factor between the K removed by the crops and the active K lost from the soil is  $0.722 \pm 0.016$ . J. J. SKINNER

A pertinent review of the fertilizer industry's development. H. D. RYAN. *Fertilizer Green Book* 6, No. 4, 13-7(1925).—A review with particular reference to the phosphate industry. K. D. JACOB

Fire insurance and the fertilizer industry. D. T. HUBBARD. *Fertilizer Green Book* 6, No. 4, 19-22(1925).—Fertilizer materials are classified according to their fire hazard, and the underwriter's instructions for storage and handling are given. K. D. JACOB

Hygroscopicity and cakiness of fertilizer materials. A. B. BEACMONT AND R. A. MOONEY. *Ind. Eng. Chem.* 17, 635-6(1925).—A comparative study was made of the hygroscopicity and cakiness of 18 fertilizer materials and 3 mixts. under conditions of temp. and humidity prevailing in Mass. during the summer season. The data show that there are significant differences between the hygroscopic values for the same substance at different humidities, and that the differences in the hygroscopicities of the different materials decrease with increase in humidity.  $\text{Ca}(\text{NO}_3)_2$  was the most hygroscopic of the materials examd. and calcined phosphate the least. In general the most hygroscopic inorg. materials are those which set hardest and the hardness of a single material usually varies with the humidity to which it is subjected. W. H. ROSS

Sulfur, sulfates and sulfides as fertilizers. G. SCHUMACHER. *Eng. Mining J. Press* 119, 769-70(1925).—Expts. of Reimer of Oregon and personal observations are cited to show the beneficial effects of S in various forms, independently of other fertilizer constituents. P. R. DAWSON

The effect of sulfur and gypsum on the fertility elements of Palouse silt loam. L. W. EADMAN. *J. Agr. Research* 30, 451-61(1925).—The Palouse silt loam has a naturally high sulfolying power and uninoculated S when added to this soil was just as efficient as inoculated S in producing sulfates. All the treatments with elementary S increased the availability of the native soil K as indicated by the increased amt. of this element in drainage water from the soils tested with S. Gypsum increased the amt. of sol. K under

greenhouse conditions but the results were indefinite under field conditions. Elemental S when oxidized in the soil in the greenhouse increased the loss of Ca in the leachings but the results obtained in the field tests were inconclusive. Both the S and gypsum treatments had little effect upon nitrification in the soil or on its H-ion concn.

W. H. ROSS

**Artificial farmyard manure.** H. B. HUTCHINSON AND E. H. RICHARDS. *Trop. Agr. (Ceylon)* 64, 24-30(1925).—The addn. of urine, urea,  $(\text{NH}_4)_2\text{CO}_3$  or peptone to a pile of damp straw produced a dark colored, structureless material resembling well rotted stable manure. This process proceeded much better when the material was freely supplied with air than when submerged in liquid. In a series of 10 expts. in which urea was added in sufficient amt. to make the total N range from 71 to 1011 mg., the total N varied only between 176 and 337 mg. after rotting 3 mos. When the added N exceeded 0.75 pts. per 100 pts. of dry straw,  $\text{NH}_3$  was lost by volatilization. When none was added atm. N was fixed until the concn. mentioned above was reached, but the process proceeded more slowly. Directions are given for mfg. this material on a large scale.

A. L. MENRING

**The making of artificial farmyard manure.** M. J. SCOTT. *New Zealand J. Agr.* 30, 91-3(1925).—Wheat, oat and barley straws were satisfactory for the production of artificial manure by the Rothamsted process, 70 tons of straw yielding about 180 tons of manure. Grass straw was not satisfactory, presumably because of its low  $\text{H}_2\text{O}$ -absorptive power.

K. D. JACOB

**Agricultural use of acid peats.** F. C. CONVILLE. *J. Am. Peat Soc.* 18, 5-7(1925).—A report of expts. showing that rhododendrons require an acid peat. C. suggests that the term "peat" be limited to those which are acid, and that the others be called muck.

J. J. WILLAMIAN

**Determination of arsenious and arsenic acids in cattle dips.** R. LAVAL. *Rev. Agr. Maurice* 2, 410-1(1925).—Prep. a soln. contg. 3.465 g. I and 6-7 g. KI per l. and standardize against pure  $\text{As}_2\text{O}_3$ . To det.  $\text{As}_2\text{O}_3$ , acidify 10 cc. of the dip with HCl to ppt. fatty acids, dil. with  $\text{H}_2\text{O}$ , add an excess of  $\text{NaHCO}_3$  and titrate with the I soln. To det.  $\text{As}_2\text{O}_5$ , dil. 10 cc. of the dip with  $\text{H}_2\text{O}$ , heat to  $80^\circ$  on the water bath, remove from it, add 70 cc. HCl and 3 g. KI. After 15 min. remove the liberated I exactly by adding 0.5 N  $\text{Na}_2\text{S}_2\text{O}_3$  soln. drop by drop, using starch indicator toward the end of the reaction. At once make alk. with solid  $\text{Na}_2\text{CO}_3$ , acidify again slightly with HCl, add an excess of  $\text{NaHCO}_3$ , and titrate. Deduct from the cc. I used in the 2nd titration that used in the 1st, and calc. the difference to  $\text{As}_2\text{O}_5$ .

F. W. ZERNAN

**Fertilizers.** J. BRESLAUER AND G. DARIER. U. S. 1,542,986, June 23. Raw cyanamide is introduced, small quantities at a time, into  $\text{H}_2\text{O}$  and the temp. is maintained at  $30-40^\circ$  while the mixt. is kept acid by the introduction of  $\text{CO}_2$  or other gaseous acids which produce insol. compds. with the metallic impurities in the raw cyanamide. By continuing the process a concd. soln. of free cyanamide is obtained which is then converted into a urea product by the use of an acid reagent such as  $\text{NaHSO}_4$ . Insol. phosphates are then introduced and the acid present is utilized for their solubilization.

**Insecticide.** WM. SCHMITZ. Can. 247,378, Mar. 3, 1925. An alkaloidal ext. of lupines is combined partly with an inorg. acid and partly with an ext. of quillaya bark or other source of saponin glucosides.  $\text{Na}_2\text{SO}_4$  may be added.

**Insecticides.** R. C. ROARK. Can. 247,562, Mar. 10, 1925. An insecticide for use with water contains BaS and S.

**Weed-destroying composition.** H. E. HUGHES. U. S. 1,543,107, June 23. A weed-killing compn. is formed from  $\text{H}_2\text{SO}_4$  20, HCl 21,  $\text{H}_2\text{O}$  18,  $\text{As}_2\text{O}_3$  9 and  $\text{KNO}_3$  2 1/4 parts.

## 16—THE FERMENTATION INDUSTRIES

C. N. FREY

**Effect of calcium sulfate on the growth and fermentation of yeast.** O. W. RICHARDS. *J. Am. Chem. Soc.* 47, 1671-6(1925).—The concn. of  $\text{CaSO}_4$  for the most efficient growth and fermentation of the yeast *S. cerevisiae* is at about 0.0001 M. Higher concns. of the salt inhibit growth and fermentation and lower concns. are inadequate for the best growth and fermentation. The concn. of  $\text{CaSO}_4$  in water supplies is usually greater than the optimum for the yeast and may occasionally be 50 times as great.

C. J. W.

**Action of alcohol upon the elective faculty of yeasts in the fermentation of grape musts.** LUCIEN SEMICHON. *Compt. rend.* 180, 1292-4(1925); cf. C. A. 17, 2628.—

Alc. exercises an important action upon the elective faculty of yeast, and the zymase function appears more sensitive to alc. than to glucose. By regulating the amt. of alc. present, very different quantities of glucose or of levulose may be consumed or conserved and the quantity of secondary products of fermentation in the wine is affected. These facts have an important relation to the organoleptic qualities of sweet wines and upon the transformations which accompany their aging. L. W. RIGGS

The occurrence and origin of acetylmethylcarbinol in vinegar. FR. VISSER 'T HOOFT *Chem Weekblad* 22, 272-6(1925) — Acetylmethylcarbinol is always contained in raisin and wine vinegar, generally in any vinegar prepd. by the Orleans or Boerhaave method from fermented fruit juices. It is mainly an oxidation product of 2,3-butylene glycol under the influence of AcOH bacteria. A small part may be formed by carbolic condensation of AcH. Since it is never present in quick vinegar and essence vinegar the Ni dimethylglyoxime reaction is a good qual. and quant. means of detg. the quality of com. vinegar. MARY JACOBSEN

Application of the thermometer in the manufacture of vinegar. HANS EGGERBRECHT *Deut. Essigind.* 29, 167-8(1925) — A discussion of the various operations involved in the manuf. of vinegar to which the temp. control plays a most important part. W. O. E.

The removal of acid from wort and from wine. M. M. L. MOREAU and H. VINET *Rev. chim. pura applicada* [3], 1, 152-9(1924) — Excessive quantities of acid are removed by the addition of powdered  $\text{CaCO}_3$  or  $\text{K}_2\text{H}_2\text{C}_2\text{O}_4$ . M. H. SOULE

Bacteriological control of beer. H. SMEETS. *Bull. assoc. école sup. brasserie Louvain* 25, 121-5(1925). A. PAFINZAU COUTURE

#### Methods for analysis of fats and wines (ANON.) 27.

Denaturing spirit. AKTIESELSKAPET SPRITDENATURERING. Norw. 40,082, March 2, 1925. The addn. consists of petroleum distn. fractions between 50 and 130° mixed in proportions that about 1/4 of it or more will boil near the b. p. of the spirit in question.

Apparatus for dealcoholizing beverages. C. H. CASPAR. U. S. 1,541,789, June 16. A cool gas is used to take up alc. from a film of the liquid to be dealcoholized and the alc. is then absorbed from the gas by a cold spray of low wines or other liquid.

Rachifying column adapted for distilling alcohol, etc. E. A. BARRET. U. S. 1,541,912, June 16.

### 17—PHARMACEUTICAL CHEMISTRY

W. O. EMERY

Examination of Peru balsam in connection with the analysis of a sample of Surinam balsam. F. HOLLMAN and P. VAN DER WIELEN. *Pharm. Weekblad* 62, 587-93(1925) — The Peru balsam from Surinam gave the following const.:  $d_{40}^20$  1.1285,  $n_{40}^20$  1.5590, acid no. 72.4, sapon no. 165.7, ester no. 93.3, cinnam. 46.1%, sapon no. of cinnam. 239.1, resin esters 16.4%, insol. in  $\text{Et}_2\text{O}$  3.55%. It differed from other Peru balsams mainly in the formation of cinnamic acid crystals when dried on the water bath. A. W. DOX

Estimation of the total alkaloids of opium. L. BARTHE and E. DUFILO. *Bull. soc. pharm. Bordeaux* 63, 95-102(1925) — Ext. 5 g. of powdered opium in a 200 cc. separatory funnel with 100 cc. of  $\text{H}_2\text{O}$  made acid with 15 cc. of 1 N HCl. Dissolve in the liquid 0.5 g. of  $\text{NH}_4\text{Cl}$  and sat. with ether by adding small quantities of the latter and shaking vigorously. Run in  $\text{NH}_4\text{OH}$ , 10 drops at a time with shaking, until the odor of  $\text{NH}_3$  becomes permanent. The excess of  $\text{NH}_3$  should be just sufficient to make the liquid alkaline to litmus paper. At the end of 24 hrs. decant the liquid contg. the crystals of morphine on a folded double filter consisting of two counterbalanced filters. Moisten the filter with distd.  $\text{H}_2\text{O}$  before decanting the liquid and also wash the separatory funnel with a little distd.  $\text{H}_2\text{O}$  after the liquid has been decanted. Pour the washings on the ppt. on the filter. Pour the filtrate into a 150-cc. porcelain capsule, add glacial AcOH until the reaction is acid to litmus and evap. the liquid to approx. 30 cc. on a water bath. During evapn. add a few drops of AcOH every 15 min. to replace that lost. Filter the liquid and wash the capsule with sufficient  $\text{H}_2\text{O}$  to bring the vol. of the filtrate to 50-60 cc. Make the filtrate alk. to litmus with dil. KOH. Stir vigorously to prevent the agglomeration of the ppt. which forms. Finally cover the beaker and set it

aside for 3 or 4 hours. Shake vigorously, pour the liquid and ppt. on the double filter and collect the filtrate in the capsule used previously. Again add AcOH to the filtrate and evap. to 15 cc. After 2 hrs. filter through a single filter and wash. Ppt. the alkaloids with KOH soln. and collect the ppt. on the double filter. Wash the total alkaloids on the filter free from chlorides and acetates of Na and NH<sub>4</sub> by means of a satd. aq. soln. of the total alkaloids obtained in a previous assay. Dry the filter and contents in an oven at 100°, cool in a desiccator over H<sub>2</sub>SO<sub>4</sub> and weigh. A. G. DuMEZ.

Oil of cade. Its preparation and density. R. MASSY *Bull. soc. pharm. Bordeaux* 63, 109-111 (1925).—M. confirms his earlier observations (*C. A.* 16, 4006) and concludes that densities lower than 1.0 are observed only in oils prepared from selected parts of the tree, such as the heart wood, which is the part sought after by the distillers because it gives the largest yield. A. G. DuMEZ.

Constituents of some Indian essential oils. XVII. Abietic acid from the resin of *Pinus longifolia*, Roxb. MADHAR GOPAL RAU AND J. L. SIMONSEN *Indian Forest Records* 11, 207-14 (1925).—Rosin acids belong apparently to 2 distinct groups: (a) the abietic acid group, members of which on dehydrogenation with 5 yield retene, and (b) a 2nd group of which pimaric acid is the chief representative which on dehydrogenation yields a hydrocarbon C<sub>14</sub>H<sub>14</sub>, probably a dimethylphenanthrene. The acid isolated from *P. longifolia* is identical with abietic acid present in *P. palustris*. New derivs., the prepn. and purification of which are described in detail, comprise a dihydrochloride, m. 205°, a monohydrochloride, m. 197°, a monohydroxy acid, m. 230° and a dimolecular hydrochloride, decomp. about 310°, and having the compn. C<sub>19</sub>H<sub>29</sub>O<sub>2</sub>Cl. The monohydroxyabietic acid is like abietic acid a very weak one and yields a methyl ester, m. 110°. W. O. E.

Odors and flavors of mints. E. M. HOLMES *Perfumery Essent. Oil Record* 16, 146 (1923).—A discussion of the more important varieties and strains of peppermint and spearmint as produced in different countries. W. O. E.

Anthranols in rhubarb. ALEXANDER TURATZ *Pharm. Monatshefte* 6, 77-9 (1925).—Rhubarb rhizomes harvested during very cold weather in the winter yielded characteristic reactions and sublimates of anthranols, one of which was identified as chrysophanic anthranol, m. 202-3°. Since C<sub>14</sub>H<sub>8</sub> yields with Se-H<sub>2</sub>SO<sub>4</sub> the same color reaction as anthranols, and since the former is used in extg. the latter, corresponding care must be exercised in applying the test. W. O. E.

Opium and cocaine problem. ERICH KNAFFL *Pharm. Monatshefte* 6, 79-83 (1925).—An address. W. O. E.

Decoctum radices senegae. K. A. KARSMARK *Pharm. Zentralhalle* 66, 333-6 (1923).—A new method is described for prepg. this decoction of a saponin of strength twice that of the original prepn., in anticipation of the Swedish Pharm. now under revision. W. O. E.

Iodine content of Jotifil. F. THEDANN *Pharm. Ztg.* 70, 660 (1925).—No free I was found in the prepn. The greater portion of the I (about 72%) is in loose combination with the protein carrier and may be split off in whole or part by the action of H<sub>2</sub>O or dil. Na<sub>2</sub>CO<sub>3</sub> soln., the remainder being more firmly combined. The analytical results of several samples are reported. W. O. E.

Adulteration of flores cinæ. R. A. FELDHOFF *Pharm. Ztg.* 70, 661 (1925).—Several notable cases are cited in which spurious *Artemisia maritima* was offered for the genuine product. In the evaluation of flores cinæ recourse was had to the property of santonin to yield an intensive red color with alc. KOH soln., the santonin-free drug imparting to the KOH soln. a yellow to greenish yellow color. If weighed amts. of the sample are extd. with alc. KOH soln. and comparison be made with other standardized exts., a colorimetric method is readily available. Of other quant. procedures the following is favored: Exhaust 10 g. of the ground sample in a Soxhlet app. with Et<sub>2</sub>O, evap. the solvent, dissolve the residue in 6 to 7 g. of 90% alc., heat to boiling under a reflux, gradually adding 25 to 30 g. of hot H<sub>2</sub>O and continuing the boiling 5 to 10 min. Filter the hot soln. 3 times through small pledgets of cotton, washing the latter twice with 10 cc. of 15% hot alc. and once with 10 cc. of boiling H<sub>2</sub>O. Receive the aq. soln. in a sep. beaker. Heat the alc. soln. again to boiling and ppt. the resins with 1.5 to 3 cc. of Pb(OAc)<sub>2</sub> soln. (1:10), passing the boiling liquid through a folded filter. Wash the ppt. with the hot aq. soln. previously reserved. Ext. the combined filtrate with 60 cc. of CHCl<sub>3</sub>, pass the latter through a filter moistened with CHCl<sub>3</sub> and distil the solvent. Ext. the residual varnish of santonin and resin with 35 to 40 cc. of boiling 15% alc., filter and wash the latter twice with 5 to 6 cc. of boiling 15% alc. Let stand 24 hrs. in a cool room, transfer the sepd. santonin to a tared filter, washing the flask and filter twice with 15% alc., then dry and weigh. W. O. E.

**Alkalinity and tinned lead tubes.** KLÜNDER. *Pharm. Ztg.* 70, 732(1925).—The tooth paste contg.  $\text{KClO}_3$  in contact with tinned leaden tubes rapidly acquired a brown color owing to the formation of  $\text{PbO}_2$  from too great alkali. A suspension or soln. of 2 g. of the paste in 20 g. of  $\text{H}_2\text{O}$  should on the addn. of 5 drops of phenolphthalein soln. show only a rose to light red coloration in the supernatant liquid. W. O. E.

**Belladonna instead of dwarf elder root.** H. JESSER. *Pharm. Zentralhalle* 66, 337(1925).—A sample of dwarf elder root was found to contain admixed belladonna root. W. O. E.

**Travancore essential oils. V. Essential oil from *Ageratum conyzoides*, Linn. (Appa grass.)** KRISHNAN LAI MOUNCHILL. *Quart. J. Indian Chem. Soc.* 1, 273-6(1925); cf. C. A. 19, 1176, 1751.—The dark brown heavy oil obtained by steam distn. of the freshly cut plant (moisture 87%) in a yield of 0.02% had the following characters:  $n_D^{25}$  1.5230,  $d_4^{25}$  1.008, acid value 0, ester value 17.4, Ac value 45.6. When distd. under reduced pressure a major fraction was obtained having the characters:  $b_{10}$  254-6°,  $b_{11}$  130-5°,  $d_4^{25}$  1.019,  $[\alpha]_D^{25} = 0^\circ$ ,  $n_D^{25}$  1.5298. The elementary analysis indicates the compn.  $\text{C}_{15}\text{H}_{24}\text{O}_2$ . Judging from the properties and constn. the compd. appears to be an oxide, but this question is still under investigation. W. O. E.

**Titration of alkaloids.** H. BAGGESGAARD-RASMUSSEN AND SV. AA. SCHOU. *Z. Elektrochem.* 31, 189-99(1925).—Of the alkaloids examd. strychnine, brucine, morphine, codeine and atropine are best titrated with methyl red, cinchonine with the same indicator under a  $pH$  of about 5.8. Quinine, being a monacid base, was detd. with  $p$ -nitrophenol as indicator. Narcotine was titrated with methyl orange,  $pH$  about 4.5. Hydrastine is difficult of exact titration, but fairly good results are obtained with methyl red,  $pH$  about 4.8. Very complete expl. data are presented in tabulated form together with titration curves. W. O. E.

**Aims and development of the medicinal and poisonous plant investigations gardens, South Dakota State College, Division of Pharmacy.** ANTON HOGSTAD, JR. *Am. J. Pharm.* 97, 325-50(1925).

**Iodole from a new source. Its properties.** JOSEPH MICHELMAN. *Am. J. Pharm.* 97, 350-52(1925).—A description of the prepn. and the properties of "Iodole" (tetraiodopyrrole). It is synthesized from pyrrole, which in turn is obtained from the destructive distn. of scrap leather (cf. C. A. 19, 1206, 1790, 2258). W. G. GAESSLER

**A new group of disinfectants. I. Chloronal.** L. PANETH. *Klin. Wochschr.* 4, 552(1925).—Chloronal is a yellow brown powder which forms a colloidal soln. with water. A 5% soln. is easily obtained. Its chem. constitution is unknown. 1:10,000 diln. kills streptococci within 1 hr. 1:100,000 diln. kills cholera vibrio in 1 hr. 1:1000 diln. is required for the colon typhoid group. It is active only in acid soln., ppts. protein, is non-poisonous, almost odorless and inexpensive. MILTON HANKE

**Oil of cinnamon leaves.** L. S. GLITCHITCH. *Parfums de France* No. 27, 117-30 (May, 1925).—In oil of cinnamon leaves were found *l*- $\alpha$ -pinene, *l*- $\beta$ -phellandrene, dipentene, benzaldehyde, free linalool, *l*- $\alpha$ -terpineol (free and combined), *l*-borneol (free and combined), geraniol (free and combined),  $\Delta^1$ -menthenone-3(?), safrol,  $\alpha$ - and  $\beta$ -caryophyllene, a *d*-sesquiterpene (*d*-caryophyllene?), eugenol (largely free, but a small quantity combined), phenylpropyl alc.(?), cinnamaldehyde, cinnamyl alcohol, cinnamonal (I) (new), foliol (II) (new), combanone (III) (new), benzyl benzoate, traces of unidentified alcs., combined  $\text{C}_{15}$ - $\text{C}_{17}$  acids, and traces of a paraffin. I, II and III are, resp., primary, secondary and tertiary, isomeric alcs.,  $\text{C}_{15}\text{H}_{26}\text{O}$ . I is a thick, amber-colored oil, with agreeable and persistent odor,  $b_p$  130-5°,  $d_4^{25}$  0.9753,  $[\alpha]_D^{25} = -30^\circ$  40'.  $n_D^{25}$  1.513, mol. refraction 68.41, which indicates a bicyclic compd. with one double bond. With  $\text{CrO}_3$  in  $\text{AcOH}$  it gives an aldehyde of strong, undefinable odor; semicarbazone could not be purified for lack of material. Oxidation in the cold with the theoretical quantity of  $\text{KMnO}_4$  gave an oily acid, heavier than water, which could not be purified sufficiently (owing to lack of material) to yield a  $\text{Ar}$  salt from which reliable figures could be obtained. II is an amber-colored oil, thicker than I, with a similar but weaker odor,  $b_p$  133-5°,  $d_4^{25}$  0.9729,  $[\alpha]_D^{25} = -15^\circ$  50',  $n_D^{25}$  1.514, mol. refraction 68.63, which indicates a bicyclic sesquiterpene alc. with one double bond. III is a highly viscous, amber-colored oil, with a slight waxy odor,  $b_p$  115-6°,  $d_4^{25}$  0.9687,  $[\alpha]_D^{25}$  practically nil,  $n_D^{25}$  1.50602, mol. refraction 68.08, which indicates a bicyclic sesquiterpene alc. with one double bond. Heating with concd.  $\text{HCO}_2\text{H}$  gives an intense violet color, and III is dehydrated to the corresponding sesquiterpene, combanone (new) ( $\text{C}_{15}\text{H}_{24}$ ) (IV). After rectification over Na, IV is a colorless oil with a faint odor recalling hydroxycitronellal, giving red, oily, uncrystallizable  $\text{HBr}$  and  $\text{HCl}$ ,  $b_p$  126-7°,  $d_4^{25}$  0.9207,  $[\alpha]_D^{25}$

—28° 20',  $n_D^{16}$  1.5106, mol. refraction 66.25 (calcd. 66.15). I, II and III all give oily phenylurethans. *Detn. of eugenol* in oil of cinnamon leaves by heating at 100° with 3.5–15% NaOH gives results 2–25% higher than shaking 15 min. at room temp. with 3% NaOH. Results by the latter method check closely with those of Thoms' method (based on the quant. transformation of eugenol into benzoyl-eugenol, which is recrystd. and weighed). The non-phenolic portion of the oil contains a small proportion (about 2% on the original oil) of combined eugenol, and a large proportion of esters of lower fatty acids and especially of BzOH. The high results obtained with NaOH at 100° are due to sapon. of part or all of these esters. Thoms' method can be used occasionally as a control method, but on account of its delicacy and length is not practical for routine and com. work.

A. PAPINEAU-COUTURE

*Oil of Ocimum canum* Sims. *ETABLISSEMENTS A. CHIRIS Parfums de France* No. 27, 139 (May, 1925); cf. C. A. 19, 703, 1032.—Previously examd. samples from Comores and Bambari (Congo) contained 54–6 and 78%, resp., of Me cinnamate. A second sample from Bambari showed  $d_4^{20}$  0.9134,  $[\alpha]_D^{20} + 3^\circ 36'$ ,  $n_D^{20}$  1.49490, does not solidify, acid no. 0.22, ester no. 101.15, esters (as Me cinnamate) 29.26%, sol. in 0.5 vol. of 85% alc. with slight cloudiness at 3 vol., sol. in all proportions with 90% alc. The low Me cinnamate content is due to the fact that the oil was produced from young plants. It is noticeable that the oil remains d-rotatory, while all the samples from Comores were l-rotatory; this may be due to absence of linalool in the Bambari samples, while the Comores samples contain 25–30% l-linalool.

A. PAPINEAU-COUTURE

*Lemon-grass oil from Central Africa*. *ETABLISSEMENTS A. CHIRIS Parfums de France* No. 27, 139 (May, 1925); cf. C. A. 19, 873, 1178.—A sample from Bambari (Congo), distd. from plants 1 yr. old, had  $d_4^{20}$  0.8853,  $[\alpha]_D^{20} 0^\circ 50'$ , citral (as bisulfite) 75%, sol. in 0.4 vol. of 85% alc., 0.1 vol. of 90% alc. and 0.1 vol. of 95% alc., with turbidity on diln. in each case. The d. and citral content are still lower than in the oil from the 2-yr.-old plants, but the soly. is unchanged.

A. P.-C.

*Chemical composition of an hybrid of Aconitum anthora L. and A. napellus. A. GORIS AND M. METIV. Compt. rend. 180, 1282–4 (1925); cf. C. A. 19, 1756.*—The roots of the above-named species differ widely in anatomical structure and also in the alkaloids which they contain. *A. napellus* yields aconitine and *A. anthora* yields anhydroaconitine and pseudo-anthorine. In structure the "hybrid of Randou" resembles *A. napellus* above ground and *A. anthora* in its root. The entire plant was dried and extd. for alkaloids in the usual way, and the product was tested by injection into guinea pigs. The animals exhibited the symptoms of anhydroaconitine poisoning followed by the symptoms of aconitine poisoning.

L. W. RIGGS

*Alteration of solutions of aconitine during aging. A. GORIS AND M. METIV. Compt. rend. 180, 1443–5 (1925).*—Sols. of aconitine lost an appreciable amt. of their toxicity within 1 week. Guinea pigs tested with a dil. soln. of aconitine nitrate which had stood 4 months showed the soln. to have less than  $\frac{1}{4}$  the toxicity of a freshly prepd. soln. The decrease in toxicity is regular and shows a practically straight line graph. The diminution in toxicity of an alc. soln. of aconitine nitrate is notable but less than that of an aq. soln.

L. W. RIGGS

*Quality of nitrous oxide manufactured in the U. S. G. W. HOOVER. J. Am. Med. Assoc. 84, 1472–3 (1925).*—Fourteen samples of  $N_2O$  gas were tested for compliance with U. S. P. requirements, and were subjected to rigid further examn. for the presence of  $NO$ . None of the samples contained sufficient impurities to warrant action under the Food and Drugs Laws.

L. W. RIGGS

*Identification of the constituents of laudanum. ALOY AND VALDIGUIÉ. J. pharm. chim. [8], 1, 369–71 (1925); cf. Guerbet, C. A. 16, 4298.*—To detect saffron, add 2 cc. HCl to a 1% aq. soln. of laudanum and shake out with 10 cc. AmOH, evap. part of the (yellow) soln. and obtain an indigo blue color with concd.  $H_2SO_4$ ; the test is sensitive to a diln. of 0.2%. To test for meconic acid, shake the remainder of the AmOH soln. with dil. slightly acid  $FeCl_3$ , which turns red. Test for morphine in the aq. soln. after sepg. AmOH. Render acid, shake out with  $Et_2O$ , render alk. with  $NH_4OH$  and ext. with  $EtOAc$ . Evap. and test the residue for morphine, best with Lafon's reagent ( $NH_4$  sulfoselenite) which produces an intense green.

S. WALDBOTT

*Determination of the hydrophilic and absorbent powers of cottons. M. PICON. J. pharm. chim. [8], 1, 380–4 (1925).*—In addn. to the Codex assays, apply the following practical tests: To det. the hydrophilic power, cut from a layer about 2 cm. thick, a prism 2 cm. sq. of about 0.1 g. wt., put it upon  $H_2O$  of exactly 15° and note the time required for complete satn. of all fibers and the moment of sinking. The best cotton (with 0.23%  $Et_2O$ -sol. matter) required 3 sec., the poorest (0.73%  $Et_2O$  sol.), 3 min.

av., about 1 mm. Temp. has a decided, but irregular influence; alkalis also affect results, with  $H_2O$  contg. 0.5% NaOH, the time is only 0.1 of that with pure  $H_2O$ . For detg. the absorbing power, place a cotton prism 5 cm. sq.  $\times$  1.5 cm., wt. 5 g., on a glass plate, keep it for 5 min. in  $H_2O$  at  $15^\circ$ , then remove and place on top of it a glass plate and wts. to a total of 500 g., while a strip of filter paper placed within 1 mm. of the cotton, and projecting beyond the edge of the plate, conducts away the excess of  $H_2O$ . After about 10 min., wipe dry the glass around the cotton, and weigh. The results confirm those of Gay, i. e., 1 g. of cotton will absorb a min. of 17 g. of  $H_2O$ , but the method used is accurate to within 5% (Gay, 10 to 25%). S. WALDBOTT

Report of the 14th Subcommission of the Codex. FABRE, J. *pharm. chim.* [S], 1, 400-7, 433-47 (1925).—A summary of proposed pharmacopoeial requirements, chem. tests and assays of powd. glands and organs. S. WALDBOTT

The Carrel-Dakin solution, E. FLEURY, J. *pharm. chim.* [S], 1, 424-8 (1925).—A table is given showing for each % of available Cl from 20 to 37% in  $CaOCl_2$  the amt. in g. to be used of  $CaOCl_2$ , anhyd.  $Na_2CO_3$  or  $NaHCO_3$  in order to prep. 10 l. of Dakin soln. contg. 0.45-0.50% NaClO. Full directions for the prepn. and use of the test solns. are given. S. WALDBOTT

Necessity of frequently titrating cherry laurel water. E. CHAUVIN, J. *pharm. chim.* [S], 1, 428-9 (1925).—Com. samples contained as high as 123 mg. and 144 mg. of HCN per l. in place of 100 mg. required by the Codex. They were prepd. of over-strength to allow for deterioration. S. WALDBOTT

New Cl bleaching compound (DE PUTTER) 18. Electrochemical preparation of theophylline (YOSHIKAWA) 4. Dissolving Br (U. S. pat. 1,541,910) 18.

Hager's Handbuch der Pharmazeutischen Praxis. Vol. I. Revised and enlarged. Edited by G. Frenichs, G. Arends, and H. Zörnig. Berlin: Julius Springer. 1573 pp. G. M. 57. Reviewed in *Pharm. J.* 114, 548 (1925).

JANSEN, SAMLET AV EDNAK. Folkenavne Paa Laegemidler Og Deres Oprindelse. 2nd ed. Kристиана Norges Farmaceutiske Forening. Reviewed in *Am. J. Pharm.* 97, 365 (1925).

Benzoxarolon-5-arsonic acid. L. BENDA. U. S. 1,543,544, June 23. By the reaction of phosgene on 4-amino-3-hydroxyphenylarsonic acid in  $NaOAc$  soln., a colorless cryst. substance is obtained, slightly sol. in cold and readily sol. in hot  $H_2O$ , difficultly sol. in alc., insol. in ether, easily sol. in alkalis at low temps. It is useful as a prophylactic and therapeutic against spirochetes.

Arseno compounds. W. KOLLE. Can. 246,556, Mar. 10, 1925. Products obtained by combining with arsenobenzenes, sulfoxylate compds. of amines which are not arsenobenzenes, are readily sol. in water, more stable than their components and have a dosis tolerata considerably larger and consequently a toxicity considerably smaller than is calcd. from the dosis tolerata of the components, while their therapeutical value is not considerably diminished.

$\beta$ -Diethylamino-4-methoxyphenetole. H. HAHLE. U. S. 1,543,287, June 23.  $Et_2NCH_2CH_2OC_6H_4OMe$ , obtained by reaction between Na 37 in alc. 50,  $HOC_6H_4OMe$  20 and  $ClCH_2CH_2NEt_3$ , is an oily substance, forming a white cryst. hydrochloride, m.  $121-2^\circ$ . It is useful in the treatment of heart diseases.

Therapeutic albumin dye compound. O. BALLY. U. S. 1,543,543, June 23. An albuminous compd., c. g., yeast, is treated with a thiazine dye, c. g., methylene blue, to form an albumin leuco dye compd. and the latter is oxidized to convert it into an albumin dye compd. which is suitable for use as a bactericide or therapeutic agent.

Medicinal carbon. J. N. A. SAUER. U. S. 1,542,006, June 16. Medicinal tablets are formed of a binder such as sucrose or lactose and a sterilized decolorizing vegetable C, substantially free from sol. ash-forming constituents and contg. over 94% free C.

Hypochlorite solutions for disinfecting. A. WOLFF. U. S. 1,542,928, June 23. A neutral or only slightly alk. soln. of  $MgCl_2$  or other chloride capable of forming a hypochlorite is treated with  $O_3$  to the point of saturation in the presence of a metal oxide such as Fe oxide. The treatment is repeated and conducted over a considerable time, c. g., several days.

Curing tobacco. A. C. BRENSON. U. S. 1,543,235, June 23. Tobacco is treated in darkness with air currents having a temp. of about  $22-27^\circ$  and a relative humidity of 75-82% and the temp. is gradually raised to about  $32-37^\circ$  without changing the relative

humidity, until the surplus food content in the leaf has been consumed and the cells have died. The temp. of the air currents is then further increased to about 45–50° without changing the relative humidity and the temp is then lowered to about 25–30° and the humidity raised to 80–85% until the necessary moisture is supplied to avoid breakage of the tobacco in handling.

## 18—ACIDS, ALKALIES, SALTS AND SUNDRIES

FRED C ZEISBERG

Reaction between arsenious anhydride and chlorine. LIVIO CAMMI *Giorn. chim. ind. applicata* 6, 527–32(1924).—The direct oxidation of  $As_2O_3$  by  $Cl_2$ , instead of  $HNO_3$ , has these advantages: greater simplicity of app., spontaneity of the reaction, since this is exothermic; a rapid and practically quant. absorption of  $Cl_2$  under proper conditions. In the oxidation the  $Cl_2$  is led into an aq. suspension of 70–80%  $As_2O_3$  with agitation, at a temp. of 60–70°, and with proper means for condensing vapors as  $AsCl_3$ . About 70% of the  $As_2O_3$  was changed to  $As_2O_5$ , and the rest to  $AsCl_3$ . A sketch is given of a scheme for prep. of *Ca arsenate*. ROBERT S. POSMONTIER.

Preparation of pure chlorine by the action of hydrochloric acid on an alkali chlorate. E. DUFILHO, *Bull. soc. pharm. Bordeaux* 63, 41–7(1925).—Set up a 2-l flask fitted with a 3-hole rubber stopper. In two of the holes insert S-shaped funnel tubes and in the third a condenser. On a shelf slightly higher than the funnel tubes place two 1-l bottles with stopcocks at the bottom so that the contents can be run into the funnel tubes. Into one of the bottles put 1 l of an aq. soln. contg. 80 g  $KClO_3$ . Into the other pour 500 cc.  $HCl$  (sp. gr. 1.17). Pour into the flask 200 cc.  $H_2O$  and 100 cc.  $HCl$  and pour to boiling, then run in from the bottles the  $HCl$  and the  $KClO_3$  soln., regulating the flow so that 2 vol. of the latter are added to 1 vol. of the former. The contents of the flask should be kept boiling. By this means 50 l  $Cl_2$  can be produced per hr.

A. G. DUMÉZ

Preparation of the sulfides of the alkalies and of the alkaline-earths. ROBERT HAZARD, *Rev. chim. ind.* 34, 14–7, 46–9, 78–82, 111–4, 149–50(1925).—A review

A. PAPINEAU-COUTURE

Present status of the nitrogen-fixation industry in the United States. CAMILLE MATIONON, *Chimie et industrie* 13, 845–61(1925).

A. PAPINEAU-COUTURE

The preparation of oxygen for the industry. GEORGE KASNER, *Z. angew. Chem.* 38, 405–7(1925).—This is a discussion of the practical application of Finlayson's method, in which "Plumbosan,"  $Na_2MnO_4 \cdot Na_2PbO_4$ , is heated at a temp. of 500–550°. The  $O_2$  is driven off in a current of steam at this temp., and the  $N_2$  remaining in the pores is drawn off by application of a vacuum. Air is readmitted and the cycle repeated indefinitely, the air being completely separated. Both the  $O_2$  and  $N_2$  obtained possess a high degree of purity. In this process the yield is 1 cu. m. of  $O_2$  from 5 cu. m. of air, as against 7.5 cu. m. required in the *Linde process*, and 10 cu. m. in the *BaO<sub>2</sub> process*. Most of the heat in the  $O_2$  can be recovered by drying or preheating apparatus. Another advantage is the shortness of the cycles, the steam treatment taking 5–10 min., the removal of the  $N_2$  about 5 sec. and treating with air again about 5 min. It is necessary to remove  $CO$ , both from the air and the steam before admitting them to the reaction chamber. This is usually a tubular retort.

H. STOERTZ

Concentration of argon from air by fractional liquefaction. G. R. FONDA, F. W. REYNOLDS and S. ROBINSON, *Ind. Eng. Chem.* 17, 676–8(1925).—An extension of Baly's work (*Phil. Mag.* 49, 517(1900)) to include the variation in A content showed that with liquefaction of 5–80% of the vol. of air the A content of the liquid passes from 2.35 to 1.6%, and that an equil. in compn. was attained as the gas bubbled up through the liquid. As far as they go, the results agree with Baly's.

A. PAPINEAU-COUTURE

A new acid-resisting material. J. H. WEST, *Chem. Age* (London) 12, 522(1925).—"Prodonite" is made by mixing a suitably graded acid-resisting mineral aggregate with a molten, special, hard pitch, which, at the temp. of use (up to 60–70°) remains absolutely rigid. It is completely resistant to all dil. acids, to concd.  $HCl$ , to  $HNO_3$  up to 30%, and to  $H_2SO_4$  up to 70% in the cold and up to 40% at 100°. It is somewhat more brittle than the best cement concrete, and its tensile and compressive strengths are equal to those of ordinary cement concrete. Its present and possible uses are briefly outlined.

A. PAPINEAU-COUTURE

Test of "ascarite," a carbon dioxide absorbent, as its own drier. F. W. MARSH, *J. Assoc. Official Agr. Chem.* 8, 442–4(1925).—Expts. are described which confirm the findings of Stetser and Norton (*C. A.* 12, 2076) that "ascarite," a special mixt. of  $NaOH$

and asbestos, requires no additional drier if the running time of the deto. is relatively short (up to 5 hrs.); but where long runs are necessary, *e. g.*, in the detn. of  $\text{CO}_2$  production from soil, ascarite loses an appreciable quantity of  $\text{H}_2\text{O}$ . A. P. C.

The water content of decolorizing carbons. WERNER MECLENBURG. *Chem.-Zig.* 49, 429-30 (1925).—If a com. decolorizing C contg. (as received) 84%  $\text{H}_2\text{O}$  be dried in air between filter paper, its decolorizing power (based on dry substance) remains const. throughout the drying. If, however, the drying be carried out at  $120^\circ$ , samples removed periodically show that when the  $\text{H}_2\text{O}$  has been reduced to 50% the decolorizing power (on dry substance) has decreased to 69% of its original value; on further drying, however, an increase takes place so that at 0%  $\text{H}_2\text{O}$  the original value has been regained.

WM. B. PLUMMER

A rapid quantitative method for determining the decolorizing power of carbons. D. S. CHAMBERLIN AND M. R. BUCKLEY. *J. Oil & Fat Ind.* 2, 4-8 (1925).—Methods for the detn. of the decolorizing power of C depending on removal of dyes from soln. are inaccurate because the end point is obscured and not permanent, and the particle size is not considered. A procedure based on the removal of I from soln. and a titration of the residual I by  $\text{Na}_2\text{S}_2\text{O}_4$  is recommended as accurate and not requiring a color comparator. The sample is ground to pass through a 300-mesh sieve, dried 5 hrs. at  $105^\circ$  and 0.5 g. weighed into a beaker, then 490 cc. of water and 10 of 0.2 N I in KI are added. The soln. is stirred 3 min., filtered through cotton and in 250 cc. of filtrate the I is detd. by titration. A blank without the C is always run with each series. Slight variations in temp. at approx.  $20^\circ$  have no effect. H. S. B.

A new chlorine bleaching compound. BARRINGTON DEPUYSTER. *Color Trade J.* 16, 137-40 (1925).—Na *N*-chloro-*p*-toluenesulfonamide (chloramine T) is being prepd. as a by-product from the manuf. of saccharin for use as a disinfectant, bleaching agent and detergent for textiles, and in the solubilization of starch. It is sold as *acifine*, *samberein*, *mannolite*, *gensil*, *glekosa*, *purus* and *Washington bleach*. Its uses in the textile industry are described. CHAS. E. MULLIN

Sulfuric acid. O. BEZANSON. U. S. 1,542,488, June 16. In making  $\text{H}_2\text{SO}_4$  by the contact process, steam is fed from a boiler into heat-transfer relation to relatively hotter sulfurous gases and the steam, thus superheated, is returned to the boiler for utilization of its heat in generating additional steam.

Recovering hydrocyanic acid from gaseous mixtures. O. LIEBKNECHT. *Can.* 247,475, Mar. 10, 1925. The gaseous mixt. is passed through activated charcoal or activated silicic acid to remove the HCN.

Production of hydrogen and phosphoric acid. F. G. LILJENROTH. *Can.* 247,164, Feb. 24, 1925. A phosphatic material is reduced with C to produce essentially P and CO, which mixt. is acted upon with water to liberate H. The  $\text{P}_2\text{O}_5$  may be removed and the remaining CO acted upon with steam to produce further H. Cf. C. A. 19, 1330.

Manufacture of ammonia from gases containing hydrogen cyanide. NORSK HYDRO-ELEKTRISK KVAELSTOF-ARTIESELSKAP. *Norw.* 40,989, March 2, 1925. The gas mixt. contg. HCN and  $\text{H}_2$  is mixed with an adequate amt. of  $\text{O}_2$  or gases contg.  $\text{O}_2$  such as air, and is then passed over a catalyzer by which the HCN is converted into  $\text{NH}_3$ .

Manufacture of solid alkali cyanide. NORSK HYDRO-ELEKTRISK KVAELSTOF-ARTIESELSKAP. *Norw.* 40,988, March 2, 1925. Gases contg. HCN are absorbed in a concd. soln. of alkali at such a high temp. that alkali cyanide will crystallize spontaneously on subsequent cooling.

Alkali metal carbonates. F. W. SPERR, JR. AND D. L. JACOBSON. U. S. 1,542,971, June 23. An alkali metal thiosulfate is mixed with  $\text{CaCO}_3$  and coal or other carbonaceous material and the mixt. is heated to form carbonate.

Ammonium nitrate. L. H. GREATHOUSE. U. S. 1,541,808, June 16. A gas contg. N oxides, which may be prepd. by catalytic oxidation of  $\text{NH}_3$ , is treated with  $\text{H}_2\text{O}$  to absorb part of the oxides and produce  $\text{HNO}_2$  and the remaining oxides are brought into absorbing contact with  $(\text{NH}_4)_2\text{CO}_3$  to produce a mixt. of  $\text{NH}_4\text{NO}_2$  and  $\text{NH}_4\text{NO}_3$  until substantially all the N oxides are absorbed. The nitrite in the soln. is then oxidized by use of the  $\text{HNO}_2$  first produced and by passing air through the soln. and the resulting N oxides are mixed with the supply from the original source.

Anhydrous magnesium chloride. ARTIESELSKAPET DE NORSKE SALTVERKER. *Norw.* 41,023, March 9, 1925. A mixt. of  $\text{MgO}$  and a carbonaceous material is treated with Cl gas at a temp. below the m. p. or the sintering temp. of  $\text{MgCl}_2$  under const. agitation of the reaction mass.

Utilization of leucite. NORSK HYDRO-ELEKTRISK KVAELSTOF-ARTIESELSKAP. *Norw.* 41,139, March 30, 1925. Leucite is dissolved in dil.  $\text{HNO}_3$  and the soln. is made

exactly neutral or slightly alk. by means of  $\text{Al}_2\text{O}_3$ . Then the liquor is evapd. to obtain on cooling mixed crystals of K and Al nitrates with an av. compn. of approx  $\text{KNO}_3 \cdot \text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ .

**Treating hydromagnesite.** W. S. RAWSON. U. S. 1,543,620, June 23. Crude hydromagnesite is stirred with a small proportion of  $\text{H}_2\text{O}$  to form a slurry, the latter is heated to about the b. p. and while hot is stirred into cold  $\text{H}_2\text{O}$  to produce a mixt. with a temp. below  $24^\circ$ . The heavier particles are then sepd. from the suspension and the latter is run through a sieve to obtain a material suitable for calcining to produce white magnesia.

**Magnesia from dolomite.** E. EVERHART. U. S. 1,542,684, June 16. Dolomite is calcined to drive off  $\text{CO}_2$ , slaked, treated with  $\text{HOAc}$  to neutralize the lime, the Ca acetate is sepd. by soln. and filtration and the residual magnesia mass is treated with  $\text{CO}_2$  to dissolve the magnesia only.

**Alumina from aluminium nitrates.** NORSK HYDRO-ELEKTRISK KVAELSTOF-AKTIENSLSKAP. Norw. 41,169, April 6, 1925. The Al nitrates are introduced in a finely divided state into a chamber through which hot gases are passed.

**Silicic acid gel.** W. J. MULLER and H. CARSTENS. Can. 427,555, Mar. 10, 1925. An insol. silicate is treated with an acid, the resulting sol is sepd. from the insol. part, allowed to gelatinize to a gel and then washed and dried.

**Iron oxide.** R. O. SNELLENBERGER. U. S. 1,542,968, June 23. Commuted Fe, treated with  $\text{FeSO}_4$  and  $\text{H}_2\text{O}$  or other reagent to accelerate oxidation, is agitated with air and periodically its temp. is reduced until oxidation is substantially completed.

**Dissolving bromine.** H. FRIEDENTHAL. U. S. 1,541,810, June 16. KCNS or other thiocyanic compds. in aq. soln. are used for dissolving Br, *e. g.*, to prep. solns. for therapeutic or industrial purposes.

**Compressing loose amorphous carbon.** G. H. WHEATLEY. U. S. 1,542,119, June 16. Mech. features.

**Phenolic condensation product.** C. B. CARTER and A. E. COXE. U. S. 1,543,369, June 23. See Can. 234,506 (C. A. 18, 450).

**"Leatherboard felt."** F. V. CHANEY. U. S. 1,541,922, June 16. Leather fiber 40, mixed paper fiber 20, coarse animal or vegetable fiber 30 and a resin size and alum or other binder 10%.

**Emulsifying benzene or other substances with wool fat.** O. HERZOG. U. S. 1,543,354, June 23. Aq. emulsions of  $\text{C}_6\text{H}_6$ ,  $\text{CCl}_4$ , camphor or other liquids insol. or difficultly sol. in  $\text{H}_2\text{O}$  are prepd. by use of either the waxy or the oily wool-fat fraction and its sulfonated product.

**Apparatus for calcining fuller's earth, etc.** C. F. SPARKS. U. S. 1,542,647, June 16.

## 19—GLASS, CLAY PRODUCTS, REFRACTORIES AND ENAMELED METALS

G. E. BARTON, C. H. KERR

**Chemical and thermal resistance of laboratory glasses.** ARNALDO MAURI. *Atti congresso naz. chim. ind.* 1924, 330-40; cf. C. A. 18, 2063.—Tests were carried out on 7 important glasses, viz., old green label Jena (I), 1920 Jena (II), 1922 Italian Murano (III), 1923 Murano (IV), original Pyrex (V), French Labo (VI) and Belgian Boromica (VII) to det. their resistance to reagents and to sudden chilling. A comparison of the quant. results with their compn. shows best the effect of various constituents. In the 1st series the glass was heated in an autoclave at  $120^\circ$  for 3 hrs. The following data give the loss in mg. with 300 cc. of soln. in 500 cc. flasks for the 7 glasses:  $\text{H}_2\text{O}$  0.5, 0.4, 0.6, 0.5, 0.4, 0.7, 0.6; 0.1 N HCl 2.6, 2.1, 2.5, 2.2, 2.0, 2.5, 2.3; 0.1 N  $\text{NH}_4\text{OH}$  9.6, 9.5, 9.5, 9.8, 9.7, 10.0, 11.2; 0.1 N  $\text{NH}_4\text{Cl}$  3.4, 2.0, 3.6, 2.0, 1.8, 2.1, 3.6; 0.1 N  $(\text{NH}_4)_2\text{CO}_3$  3.7, 4.0, 3.5, 3.5, 4.2, 4.1, 4.3; 0.1 N NaOH 81.1, 123.0, 80.5, 107.8, 229.0, 84.3, 82.0; 0.1 N  $\text{Na}_2\text{PO}_4$  12.0, 9.0, 10.5, 11.5, 13.5, 10.8, 10.7; 0.1 N  $\text{Na}_2\text{CO}_3$  45.6, 72.0, 44.0, 68.0, 101.3, 47.2, 46.0; 0.1 N  $\text{Na}_2\text{S}$  90.0, 75.2, 89.9, 81.0, 75.5, 94.1, 93.0. In further tests the solns. were boiled for 2 hrs. in the open. The losses were: N HCl 3.3, 2.0, 3.1, 2.5, 2.0, 3.1, 3.0; 0.1 N HCl—, 1.0, 3.5, 2.0, 0.9, —, —; 0.1 N  $\text{HNO}_3$ —, 0.8, 1.2, 0.9, 0.7, —, —; 0.1 N  $\text{H}_2\text{SO}_4$ —, 1.0, 1.1, 1.2, 0.5, —, —; 0.1 N  $(\text{CO}_2\text{H})_2$ , 0.1 N  $\text{H}_2\text{S}$ , satd. aq.  $\text{SO}_2$  and 0.1 N  $\text{NH}_4\text{OH}$ —, 0.0, 0.0, 0.0, —, —; N  $\text{NH}_4\text{OH}$ —, 4.3, 4.2, 2.5, 2.8, —, —; N  $\text{NH}_4\text{Cl}$  0.3, 0.2, 0.5, 0.2, 0.1, 0.4, 0.5; N  $(\text{NH}_4)_2\text{CO}_3$ —, 1.5, 1.0, 1.0, 2.0, —, —; 0.01 N NaOH 10.0, 13.0, 9.0, 10.7, 19.5, 10.5, 10.0; 0.1 N  $\text{Na}_2\text{PO}_4$ —, 1.5, 3.0, 2.3, 2.0, —, —; 0.1 N  $\text{Na}_2\text{CO}_3$  14.8, 17.6, 14.5, 17.5, 24.0, 16.3, 15.0; 0.1 N  $\text{Na}_2\text{S}$  9.5, 6.1, 6.0, 6.5, 7.4, 13.3,

12.5, 0.1  $N$   $(NH_4)_2S$  2.6, 1.6, 1.8, 2.5, 2.2, —, —. In expressing resistance to reagents, the customary units involving loss per vol. should be replaced by the more rational *loss per unit area of surface exposed*. Since evapn and ebullition cause a continual variation in this surface area, accurate resistance tests should always be done in an autoclave. It would be of great advantage if data were available for every type of glass to give *correction coeffs* which would represent the losses in various reagents at different concns and temps for a given time. In illustration of this the following data give the corrections to be applied to the 7 glasses in quant. analysis, based on a 500-cc flask with 300 cc of soln. boiled over a flame for 30 min:  $H_2O$  all 0;  $NHCl$  1.0, 0.5, 0.5, 0.4, 0.3, 1.0, 0.9;  $NH_4OH$  1.0, 1.4, 1.0, 1.3, 1.5, 1.6, 1.5, 0.01  $N$   $NaOH$  3.0, 4.5, 2.5, 4.3, 6.0, 4.2, 4.0, 0.1  $N$   $NH_4Cl$  —, —, 0.1, —, —, —, —; 0.1  $N$   $Na_2PO_4$  0.1, —, 0.1, —, —, 0.2, 0.1; 0.1  $N$   $(NH_4)_2CO_3$  —, 0.1, —, —, 0.1, —, —; 0.01  $N$   $Na_2CO_3$  1.1, 1.2, 1.1, 1.3, 1.6, 1.4, 1.2, 0.01  $N$   $Na_2S$  1.3, 1.1, 2.0, 1.2, 1.1, 2.7, 2.5. On repeating the same treatment the losses decrease progressively, so the data are comparative only. On chilling from  $150^\circ$  to  $15^\circ$ , V and IV gave excellent results, III, I, II and VII were less resistant but were good and VI was poor. The analyses showed the samples to contain in %  $SiO_2$  64.5, 75.5, 60.0, 78.0, 81.0, 67.5, 64.0,  $B_2O_3$  10.8, 8.65, 10.0, 10.0, 12.0, 5.0, 13.0;  $Al_2O_3$  4.4, 4.7, 6.4, 4.8, 2.5, 0.6, 5.5,  $ZnO$  11.1, —, 10.1, —, —, 6.0, 10.1;  $CaO$  0.6, 0.9, 1.1, 2.4, 0.0, 5.7, trace;  $Fe_2O_3$  0.2, 0.35, 0.3, 0.2, 0.2, 0.3, 0.35,  $BaO$  0.0, 4.5, 0.0, 0.0, 0.0, 0.0, 0.0;  $Na_2O$  7.5, 4.8, 6.0, 4.2, 4.5, 6.5, 7.1,  $K_2O$  0.4, 0.6, 0.0, 0.0, 0.0, 4.9, 0.0. C. C. DAVIS

**The crystallization of glasses.** Paving with crystallized basic glasses. A. BIGOT. *Rev. universelle mines* [7], 5, 246-57 (1925).—A general description of the physics and chemistry of glass, with analyses of 8 types. An illustrated description is also included of the sources and properties of basic glasses (cf. C. A. 17, 2760) from slags, scoria, etc. which have become of use as flagstone and paving materials. C. C. DAVIS

**Polymorphism and tempering of glass.** Preliminary communication. A. A. LEBENOV. *J. Russ. Phys. Chem. Soc., physical sect.* 50, 57 (1921).—There is a sudden change of properties of glass at temps  $540-600^\circ$ , as proven in the study of heating curves and changes of double refraction and coeff. of expansion with the temp. This change is attributed to a polymorphous transformation closely allied to the transformation  $\alpha \rightleftharpoons \beta$  quartz. Glasses are assumed to be an aggregation of highly dispersed crystals among which quartz crystals also are present, probably in the form of solid solns, as a result of which the transformation takes place over a certain temp. interval, the glass passing through a no. of equil. states. This explains the difference in glasses tempered at different temps and which cannot be explained by internal strains alone. Internal strains are some of the results of polymorphous transformations which are accompanied by vol. changes. Changes of the coeffs. of refraction and expansion have been studied by new methods which have been described in detail. W. M. S.

**The surface tension of molten glass.** AD. LECRENIER and P. GILARD. *Bull. soc. chim. Belg.* 34, 27-34 (1925).—For description of the app. used cf. C. A. 18, 1885. With  $SiO_2-Na_2O-CaO$  glasses the surface tension is lowered by increasing the amt. of  $Na_2O$ , by replacing  $Na_2O$  by  $K_2O$ , and by addn. of  $Na_2SO_4$  or  $B_2O_3$ . It is increased by increasing the amt. of  $SiO_2$  or  $CaO$ , or by replacing  $CaO$  by  $BaO$ ,  $MgO$ , or  $Al_2O_3$ . The fusibility and viscosity of glass. *Ibid.* 55-65.—With the use of 1 g. of broken glass in a Pt crucible with a small bottom opening, the time from its introduction into the furnace till the falling of the 1st drop is divided into the time necessary for the standard glass,  $6SiO_2-1Na_2O-1CaO$ , to give the coeff. of fusibility. Complete substitution of the  $CaO$  by  $MgO$  drops the coeff. (from 1.0) to 0.41, substitution by  $Al_2O_3$  similarly to 0.098. The viscosity number is the ratio of the time required for 1 g. to drop from a known orifice under definite conditions to the time required by the standard glass (q. v.), this time being ealed from the av. time between drops and the av. drop wt. Data for a no. of compns. are given for  $1050^\circ$  and  $1150^\circ$ . Also in *Rev. universelle mines* [7], 6, 180-206 (1925). W. M. S.

**The conductivity of annealed and unannealed soda-lime glasses.** M. J. MULLIGAN. *Trans. Roy. Soc. Canada* 18, III, 120-1 (1924).—The conductivities of annealed and unannealed soda lime glass exhibit a marked difference (approx. 200%). The conductivities are the same kind of function of the temp. in both cases, so that the change in glass brought about by annealing is one of degree rather than of kind. Data were made of the wts. of materials that were electrolyzed into these glasses at  $180^\circ$  from a molten anode ( $KNO_3$  and  $AgNO_3$ ). The amts. were approx. inversely proportional to the resistance of the glasses, but the depth of penetration of  $Ag$  ions does not bear out the assumption that there is a marked difference in the degree of ionization of the glasses. The major factor in increasing resistance by annealing is a decrease in the mobilities of the ions. H. H. S.

Brittle and elastic glasses. F. JOCHMANN. *Sprecksaal* 58, 265 6(1925). 11. G S  
Glass tank design. JAMES A. VOORMIS. *Fuels and Furnaces* 3, 167-8, 171  
(1925)—An article explaining design of combustion chambers, and calcn. of dimensions  
for ports; it is illustrated with definite figures as to temps and gas requirements. *Ibid*  
487-91—This article gives data for design of regenerators, flues and stacks, it is illus-  
trated with typical figures.

Developments in the glass industry. BJARNE SCHJELDROF. *Fuels and Furnaces*  
3, 41(1925).—A symposium of new patents on the glass making industry indicates that  
the greatest progress is shown in the plate glass industry and also that the forming dept.  
is receiving much attention, but that the melting dept. is not receiving the consideration  
it should. Ratio is as 60 13

The early glass houses of Bristol. FRANCIS BUCKLEY. *J. Soc. Glass Tech* 9,  
36-61(1925)—Historical.

A note on new ideas for tank furnace design. T. TERSEN. *J. Soc. Glass Tech*  
9, 61-71(1925).—A comparison is made of the dimensions in modern open-hearth steel  
furnaces and glass tanks. The standard type of glass tank, namely, that of the cross  
flame regenerative furnace with a melting and working end, sep'd by a fixed bridge and  
heated by the flames emerging from 3, 4 or more ports on either side of the melting end.  
It is pointed out that to improve the life of the furnace, the burners should not be di-  
rected on the side walls. Suggestions for improving the bridge design are given.

Some recent developments in furnaces for glass works. J. S. ARKINSON. *J.  
Soc. Glass Tech* 9, 72-83(1925).—A new design of pot furnace is illustrated. The gen-  
eral design follows closely the design of the "Strin" standard pot furnace. A design of  
tank furnace which was developed at the Charlton Works of the United Glass Bottle  
Co., by T. C. Moorshead is also illustrated. Instead of the rectangular melting and re-  
fining chambers as built with the ordinary design of tank furnace, the corners of these  
chambers are eliminated, giving a stream line effect. A cut shows the construction of  
a continuous leer now being installed in the north of England.

Information on window glass tank block. J. L. CRAWFORD. *Ceram. Ind.* 42,  
107(1925).—The sizes of tank blocks trued for an 8, 12, 15 and 18 in. wall are given.  
The window glass industry usually uses blocks trued for an 18 in. wall. Dimensioned  
sketches show a "throat" block for the open bridge wall and a "floater" which is used  
instead of a "throat" in window glass tanks. Several oil-fired recuperative tanks are  
in use and working satisfactorily. As long as fire clay is used for lining tanks it is doubt-  
ful whether they can be insulated successfully at the melting end. P. D. H.

Some properties of a sandstone block, after use in a glass furnace. H. S. HOULS-  
WORTH. *J. Soc. Glass Tech* 9, 3-11(1925).—A detn. of the depression of the fusion  
temp. of refractory materials when mixed with the same proportion of the same glass  
indicates their relative resistance to the solvent action of the glass. To this end the  
refractory material and the glass were ground sep. until they passed a 100 mesh screen,  
and were then thoroughly mixed in the desired proportions. Powdered Penshaw stone  
has a somewhat greater resistance to chem. attack by a soda-lime glass than has a good  
fireclay brick after powdering. Penshaw stone retains a close, compact structure when  
used in a glass furnace. This tends to hinder the penetration of glass into the stone,  
so adding to the life of the refractory material. A detn. of the depression of the cone  
fusion temp. of the powdered refractory material when mixed with powdered glass,  
taken in conjunction with the change in porosity after being fired, furnishes a satisfac-  
tory guide to the resistance to corrosion of the refractory articles exam'd. when used  
in a glass furnace. Penshaw stone as quarried showed an after-expansion of 1.4%  
after heating for 2 hrs. at cone 9 and 1.3% after being fired at cone 14. The reversible  
thermal expansion of the stone after use in a glass furnace was not very different from  
that of a fireclay brick. J. G. P.

Mechanical strength of porcelain insulators. A. O. AUSTIN. *Elec. World* 85,  
1253-5(1925).—A well designed insulator is a compromise between working load, ulti-  
mate test strength and thermal stress. A. discusses at length the various problems  
connected with the manuf. of the modern insulator. C. G. F.

Ceramics. C. C. KRAUSS. *Proc. Am. Gas Assoc.* 1924, 615-23.—A brief general  
discussion of the methods in use in the ceramic industry and of the historical develop-  
ment of the industry. WM. B. PLUMMER

Refractories for water gas sets (RUSSELL) 21.

Furnace for sheet glass manufacture. E. DELACUVILLERIE. U. S. 1,541,906,  
June 16.

Annealing glass. K. M. HENRY. U. S. 1,540,264, June 2. Glass is quickly heated to about 540°, maintained at this temp. for about 15 min. and then cooled at the rate of about 3.3° per min.

Glass furnace for drawing continuous sheets of glass. J. J. QUERTINMONT. U. S. 1,541,772, June 9.

Molding ceramic ware. R. SPRENGER. U. S. 1,541,869, June 16. Mech. features.

Apparatus for drying ceramic ware, etc. T. ALLSOP and W. W. SIMSON. U. S. 1,539,806-7, May 26.

Vitreous silica. L. B. MILLER. U. S. 1,541,584, June 9. Clear vitreous  $\text{SiO}_2$  is prepd. by heating cryst.  $\text{SiO}_2$  to a fusing temp. *in vacuo* while mechanically supporting the quartz to prevent displacement of particles resulting from the cracking of the quartz which occurs at a temp. of about 550°. Cf. C. A. 19, 1935.

Refractory product. J. T. LITTLETON. Can. 247,523, Mar. 10, 1925. A cryst. refractory product consists of fused silicate materials having a heterogeneous arrangement of crystals formed by adding particles of unmelted cryst. silicate to molten material.

Electric enameling furnace. R. E. TALLEY. U. S. 1,542,278, June 16.

Abrasive. H. R. POWER. U. S. 1,539,694, May 26. A gum, e. g., gum tragacanth, is used with carborundum or other abrasive particles for grinding engine valve seats, etc., without using either Na silicate or oil. Glycerol and basic Pb acetate may be added.

## 20—CEMENT AND OTHER BUILDING MATERIALS

J. C. WITT

Experiments on the setting of portland cement. JULES CARTIAUX. *Rev. mat. constr. trav. pub.* 184, 1-3 (1925).—The investigation included (a) detn. of free  $\text{CaO}$ ; (b) detn. of sol. salts; (c) influence of air and of  $\text{CO}_2$  on the time of set; (d) study of the loss in wt. of a mixt. of cement and distd.  $\text{H}_2\text{O}$ , due to the evapn. of  $\text{H}_2\text{O}$  and the absorption of  $\text{CO}_2$ . There was a loss of 0.5% at the initial set and 0.7% at the final set. At the end of 3 months the loss was 6%. The final reading after more than 2 yrs. showed a net loss in wt. and an increase in  $\text{CO}_2$  equiv. to 6%  $\text{CaCO}_3$ . LOUIS NAVAIS

French specifications for slag cements. ANON. *Rev. mat. constr. trav. pub.* 185, 41-2 (1925).—Slag cement consists of a mixt., properly proportioned and thoroughly mixed, of carefully slaked and bolted hydraulic lime and finely ground basic blast furnace slag, and has the following chem. and phys. properties: It shall not contain more than 5%  $\text{MgO}$ , 12%  $\text{Al}_2\text{O}_3$ , 2.5%  $\text{Fe}_2\text{O}_3$ , 2% S, 5% volatile;  $(\text{SiO}_2 + \text{Al}_2\text{O}_3)/(\text{CaO} + \text{MgO})$  not less than 0.70; fineness (4900 mesh per sq. cm.) not over 12%; (900 per sq. cm.) not over 2%; apparent density not less than 900 g. per l.; initial set, not less than 1 hr.; final set, not less than 3 hrs. Tensile strength, neat, (specimens immersed in sea water 24 hrs.) 7 days, 18 kg., 28 days, 25 kg., with an increase of at least 3 kg. between 7 and 28 days. Tensile strength, mortar, under the same conditions, 7 days, 8 kg., 28 days, 18 kg. with an increase of not less than 2 kg. Specimens kept in a moist atm. for 24 hrs., then immersed in sea water, and then maintained at 100° for 3 hrs., shall not increase more than 5 mm. between 2 needle points placed at standard distance. L. N.

French specifications for aluminous cements. ANON. *Rev. mat. constr. trav. pub.* 185, 42 (1925).—Aluminous cement shall be produced by heating a mixt. of  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{CaCO}_3$ , and grinding the product. It shall meet the following requirements: not less than 30%  $\text{Al}_2\text{O}_3$ ; not more than 2%  $\text{MgO}$  nor more than 1% S;  $(\text{SiO}_2 + \text{Al}_2\text{O}_3)/(\text{CaO} + \text{MgO})$  less than 1%; not over 20% retained on a screen of 4900 mesh per sq. cm.; an apparent density of at least 900 g. per liter; an initial set in not less than 45 min.; a final set in not more than 7 hrs.; tensile strength (specimen immersed in sea water 24 hrs.), 2 days, not less than 27 kg., 7 days, 28 kg., 28 days, 29 kg. When specimens are stored in a moist atm. for 24 hrs., then immersed in sea water, and finally kept at 100° for 3 hrs., they shall not increase in length more than 1 mm. between 2 needle points placed at standard distance. LOUIS NAVAIS

The effect of moisture on concrete. W. K. HART. *Proc. Am. Soc. Civil Eng.* 51, 757-93 (1925).—The strength of concrete varies with the moisture content. When satd. it has about 80 to 85% the strength of dry concrete. The coeff. of expansion is from 0.0000040 at 65° F. to 0.0000060 at 140° F. Concrete expands when immersed in water and contracts on drying, the change of length varying with the quality of cement, richness of mix, size of specimen, and conditions at exposure. Drying shrinkage and drop in temp. produce max. strains, while a drop in temp. and rainfall may leave the length unchanged. Concrete structures should be designed for the least favorable conditions. Requirements for concrete exposed to the weather should include cement

of volume constancy; clean, well-graded aggregate; impervious concrete of proportions not less than 1:2:4; mixing time not less than 1 min. and preferably 1.5 min.; minimum practicable quantity of  $H_2O$ ; careful slicing of the dry concrete against the face of the forms so that the reinforcing steel may not be exposed nor the surface require patching, adequate curing, depending on local conditions; design of reinforcing steel and contraction or expansion joints to prevent cracking and the entrance of water. J. C. WITT

Effect of hydrated lime and other powdered admixtures in concrete. D. A. ABRAMS. Structural Materials Research Lab., Lewis Inst., Chicago. *Bull.* 8, 74 pp. (2nd ed., 1925).—Tables and diagrams have been revised to include 2- and 5-yr. tests. See C. A. 14, 2695. E. J. C.

The significance of the common test methods for determining the strength of mortars. J. W. GOWEN AND H. W. LEAVITT. *Proc. Am. Soc. Testing Materials* 1925, (preprint) 10 pp.—A mathematical analysis of data of standard tension and compression mortar tests and a new test similar to a Deval abrasion test on 2-inch mortar cubes indicates that each of these tests gives new information concerning the properties of the mortar. RAYMOND WILSON

The effect of chlorides and sulfates on the hardening of lime mortars. ED. JUSTIN-MUELLER. *Chem.-Ztg.* 49, 390-1 (1925).—Sulfates of Mg, Al and Fe hastened hardening by the formation of complex gels. RAYMOND WILSON

Some modern gypsum products. J. M. PORTER. *Chem. Met. Eng.* 32, 499-500 (1925).—A review of progress in the use of gypsum products in construction. R. W.

Machine for the determination of the pliability of prepared roofing and the breaking point of bitumen. C. S. REEVE AND F. W. YEAGER. *Proc. Am. Soc. Testing Materials* 1925 (preprint) 5 pp.—Description of an app. to bend a roofing sample at a uniform rate over a  $\frac{3}{16}$ -inch mandrel. The angle of bend at which cracks appear is a measure of the pliability. The app. can be used to det. the breaking point of bitumen. RAYMOND WILSON

Turning calcium sulfate wastes into valuable products. G. L. MONTGOMERY. *Chem. Met. Eng.* 32, 547-51 (1925).—Manuf. of tile and stucco from  $CaSO_4$  waste at the Rumford Chem. Works is described. E. H.

The effect of the water-soluble constituents of tar oil on carbolineum. A. CARSELLI. *Chem.-Ztg.* 49, 295-6 (1925).—The author claims that the findings of Bateman (C. A. 14, 1023) that the toxicity of creosote is dependent on the water soly. of its constituents does not apply to oils for surface application such as carbolineum. The presence of water-sol. tar acids and bases in thin surface oil films is objectionable as they predicate losses by weather exposure and evapn. and cause water absorption by the oil and through the oil into the wood. A specification for carbolineum is presented. ALFRED L. KAMMERER

Crystallization of glasses (Bicor) 19. Bituminous emulsion [for roads] (U. S. pat. 1,542,626) 22.

Lime. I. WARNER. U. S. 1,542,195, June 16. Limestone is heated as it is passed through a rotary kiln to a temp. above that of dissociation and the heated mass, still above dissociation temp., is transferred to a heat-insulated chamber where it remains for a sufficient time to complete the calcination.

Lime-hardening composition. D. M. HARRISON. Can. 247,396, Mar. 3, 1925. The compn. contains a lime-waterproofing mixt., a chloride water-absorbing mixt. and iron dust.

Hardening and waterproofing composition. D. M. HARRISON. Can. 247,397, Mar. 3, 1925. The compn. contains a water-repellent material contg. lime, a mixt. of water-absorbing halogens and a metal carbonate.

Composition board. J. E. PARSONS. U. S. 1,543,394, June 23. A sheet of flexible fibrous material such as felt or burlap is immersed in a heated liquid composed of glue, shellac, resin and  $H_2O$ ; it is then removed, dried, pressed and coated with a plastic pasty mixt. of glue, whiting, resin and shellac.

## 21—FUELS, GAS, TAR AND COKE

A. C. FIELDNER

Recent developments in fuel technology. R. WIGGINTON. *Fuel in Science and Practice* 4, 183-4, 229-31 (1925); cf. C. A. 19, 2118.—Brief reviews in abstract form.

C. C. DAVIS

Smokeless fuel and oil. C. H. LANDER. *Chemistry and Industry* 44, 521-4 (1925).—A review of some of the activities of the Fuel Research Board. H. L. O.

The national liquid fuel problem in Belgium. R. BAETSLE. *Bull. assoc. inst. sup. ferm. Gand* 26; *Ann. soc. brasserieurs* 34, 191-209 (1925).—A discussion of the various aspects of the question and especially of the possible use of EtOH, of  $C_2H_6$ , and of synthetic petroleum. A. PAPINEAU-COUTURE.

The liquid fuel problem, and proposed solutions. A. TRAVERS. *Chimie et industrie* 13, 373-82, 722-30 (1925).—A discussion of the nature and distribution of petroleum, of the processes of production of motor spirits from heavy oils or coal (cracking, berginization, synthesis from gaseous C compds.), and of the situation in France. A. PAPINEAU-COUTURE.

An investigation of the behavior of solid fuels during oxidation. I. The ignition of solid fuels. BURROWS MOORE AND F. S. SINNATT. *Fuel in Science and Practice* 4, 191-8 (1925).—On the assumption that the tendency of coal to ignite spontaneously depends upon the rate of production of heat, expts. were made to det. the rate of combustion of coal under standardized conditions. The term combustible capacity is also suggested as a measure of the value of a coal. It is the capacity to evolve heat on combustion and is a function of the actual amt. of heat evolved and of the rate of this evolution. A small quantity of coal was introduced into an excess of O at a definite temp. and the increase in the temp. as a function of the time was detd. for the period preceding glowing and during the glowing stage until combustion was complete. Each coal was examd. at the min. temp. at which it eventually glowed. This glow-point was the same as the min. temp. at which the coal increased in temp. in O and was a characteristic for every coal. By plotting the temp. against the time, the curve first showed a slight depression or min. because of heat absorbed from the O, and then climbed to a max. with subsequent decline. The part of the curve from the min. through the original temp. to the glow-point was practically a straight line and its slope represented the rate of heat evolution during oxidation and before actual ignition. Its slope therefore was a measure of the relative tendencies of coals to ignite spontaneously, at least up to the glow-point. Expressed in degrees rise in temp. per sec. it is termed the ignition factor and when measured under standardized conditions should be a useful index of the tendency to spontaneous ignition. Five coals gave ignition factors of 2.5-4.9. This factor in conjunction with the area under the curve which shows the total heat evolved also serves as a criterion of the combustible capacity of a solid fuel. C. C. DAVIS.

The application of pulverized fuel to the industrial plant. W. EDWARD. *Power* 61, 784-7 (1925).—The advantages and limitations of burning pulverized fuel are reviewed. D. B. DRILL.

Motor fuel standards. ANON. *Petr. Times* 13, 884 (1925).—The German method of standardizing motor fuels introduced by the Union of Benzol Producers consists in taking the av. of the b. ps. of the fuel at every 10%, starting with 5%. The method is thought to have some value. D. F. BROWN.

Alcohol motor fuel from molasses. II. The use of alcohol and alcohol-ether mixtures as motor fuels. E. C. FRIEGLAND AND W. G. HARRY. *Ind. Eng. Chem.* 17, 717-20 (1925); cf. C. A. 19, 2119.—For const.-speed engines (stationary or tractors) alc., with 1.0% gasoline to improve starting and 0.5% aniline or pyridine to combine with acidic combustion products, is satisfactory, the vol. of fuel consumed is increased 33-50% but the thermal efficiency is unchanged or slightly increased. For automobiles the addn. of 7-15% gasoline and 0.5-0.75% pyridine gives a fairly satisfactory fuel, although the range of speed variation is not as large as with gasoline because of the narrower limits of formation of explosive alc.-air mixts. A mixt. alc. 59.5, ether 39.0, gas oil 1 and pyridine 0.5% is more satisfactory from the operating standpoint, and gave 20.5 mi./gal. as compared to 22.5 for gasoline, the thermal efficiency being somewhat higher for the former; for use in the tropics mixts. contg. as low as 20% ether are satisfactory as regards starting and speed flexibility. Miscellaneous road tests, the adjustment and revision of carburetors, and various general considerations are described and discussed. WM. B. PLUMMER.

Factors influencing carbon formation in automobile engines. J. W. ORLUP AND O. L. LEE. *Ind. Eng. Chem.* 17, 731-5 (1925).—The observation of previous workers, that C deposition in gasoline engines cannot be controlled despite the most careful regulation of test conditions, has been confirmed. By taking all possible precautions to prevent the entrance of crank-case oil into the cylinders (special and extra tight rings, special drip holes, etc.) the deposits could however be controlled. Based on an av. consumption of 1 qt. oil/150 mi. and 15 mi./gal. gasoline, and assuming 50% of the oil to be lost through leakage, the oil consumed in the cylinder would be 1.25% of the total

fuel, so that the C deposits encountered in practice are readily comprehensible. The factors influencing C deposition are therefore evidently the same as those influencing crank-case diln.

Future alcohol engines. ROBERT FORQUE *Chaleur et industrie* 6, 159-65 (1925) — A brief review of work done to the present day on the use of EtOH as fuel in explosion engines, with a discussion of the merits of EtOH, of the technic of its use, and of its possible use for internal-combustion engines.

The air oxidation of naphtha oils. B. TORDENIKOFF *Z. angew. chem.* 38, 350-1 (1925); cf. C. A. 18, 2123. — A reply to Grün (C. A. 19, 724) denying the charge of trespassing on G's scientific territory.

Cleaning of generator fires and progress towards clinker prevention. J. H. WARRICK. *Proc. Am. Gas Assoc.* 1924, 816-9 — Min clinker troubles are obtained when the ash m. p. lies between 2300° and 2500° F. higher or lower m. p. causing clinker formation, resp., on the walls or grates, for an ash m. 2200° F. the rate of blasting should not exceed 400 cu. ft./sq. ft. grate/blow, while at 2600° F. it may be raised to 550 cu. ft. No attempts have as yet succeeded in mechanically preventing clinker trouble, but from the results obtained separately with rotating grates and water cooling of the lower part of the shell, it would seem that combination of these features would be successful.

Steam accumulators. O. H. SMITH *Proc. Am. Gas Assoc.* 1924, 820-1 — A brief description of the usual type of steam accumulator or regenerator. It may be satisfactorily applied to making the blower engine exhaust steam available for use during the run in water-gas sets.

Bituminous coal as generator fuel for large water-gas sets with waste heat boilers. Wm. A. DUNKLEY. *Bur. Mines, Dept. Interior, Tech. Paper* 335, 1-43 (1925). — The tests were carried out at the Joliet plant of the Coal Products Mfg. Co.; this plant consists of 5 standard 11 ft. sets connected to 5 vertical fire-tube waste heat boilers, each of which contains 192 4-in. tubes. The sets are equipped with automatic controls and complete measuring equipment. The coals used were Murphysboro (Ill.) and Ethel (W. Va.) lump, their analyses being, resp., volatile matter 35.2, 33.3, fixed C 57.9, 54.4, ash 6.9, 12.3%; because of the handling system in use there were considerable fines in the fuel as charged into the sets, screening not being feasible. During the heat-balance period operating data were as follows. *Operating conditions*, test duration 144 hrs., continuous; 3 sets operated; cycle used, 1.9 min. blow, 0.2 min. blow run, 2.65 min. steam run, 0.17 min. air purge, all steam runs split 1.1 min. down and 1.55 min. up; coaling 2400 lbs./set/7 runs. *Results*. — Gas made 80,800 cu. ft./running hr./set, or 7609 cu. ft./run/set. Generator fuel 46.0 lbs./1000 cu. ft. gas, blown-over fuel 4.78 lbs., ash and clinker 4.20 lbs., net generator fuel 37.02 lbs. Oil used 3.72 gals., steam used 50.5 lbs., air used in generator 1970 cu. ft., tar produced 3.76 lbs., all the foregoing being/1000 cu. ft. gas made. Heating value of gas 561 B.t.u./cu. ft. *Heat balance*. — *Output data in % of input*. Finished gas, heating value 49.0, sensible heat 1.4; stack gas, combustible 11.1, sensible heat 7.9; heat in undecomposed steam 4.6; H<sub>2</sub>O in stack gas 2.7; blown-over fuel 4.8; ash pit combustible 1.2, sensible heat 0.2; steam generated in waste heat boilers 9.1; heating value of tar 5.4; sensible heat of tar 0.2; radiation and convection 1.0; total output 98.6% of the input. These results show unduly high steam consumption, stack gas combustible loss, and oil consumption. The 1st is due to channelling which necessitates much steam to prevent the top becoming overheated; regulation of the blast pressure and charging coal around the edges reduce channelling but it is still a very serious difficulty with bituminous coal in large generators. The stack gas combustible loss was high because of the fact that the tertiary air was admitted at the top of the superheater at a const. setting; having one operator to regulate this air supply for all the sets improved the efficiency considerably. The high oil consumption is due to the use of the blow run operation, which was omitted with a saving of 0.5 gal. oil/1000 cu. ft. gas, the B.t.u. being decreased by only 18. With these changes the operating results (1 month's av.) became gas made 65,500 cu. ft./running hr./set, oil used 3.17 gals./1000 cu. ft. gas, generator fuel (net) 39.98 lbs., heating value of the gas 543 B.t.u./cu. ft. These final data represent a production capacity of 39% that for coke at 42 in. blast pressure. A discussion of the economics of the situation follows. With generator coal at \$8.50/ton, boiler coal 5.50, and coke 15.00, the latter being the price at Joliet in 1922, the difference in favor of coal is 4.25 cents/1000 cu. ft. gas, despite the increase of 1.44 cents capital charges, 0.8 cents operating labor, and 1.4 cents maintenance labor and supplies.

Practical application of the use of bituminous coal as generator fuel by the Coal Products Manufacturing Co. W. J. MURDOCK. *Proc. Am. Gas Assoc.* 1924, 766-76. —

The Joliet (Ill.) plant of the above company has been operating on bituminous coals ranging from 29.8 to 35.8% volatile. Trouble with carburetor plugging was experienced at first but was eliminated by the use of a high pressure oil system with checkless carburetors; screening over 2-in. mesh reduced blow-overs from approx. 4% to under 2%. Automatic regulation of the blast pressure is important on account of the varying resistance of the fuel bed. Their schedule is 2 min. blow, 2.75-min. steam run, 0.25-min. purge, all split runs, 50% down steam; 2200 lbs. coal charged every 8 runs, the 1st blow after charging 1 min. followed by a 1-to-2-min blow run into the bolder. More combustible gas is formed during the blow than can be burned in the carburetor and superheater so that tertiary air is constantly admitted in the waste-heat boilers. Generators of small diam. with deep fuel beds are preferred so that the effect of variations in the bed may be reduced to a minimum. Complete operating data are given covering tests of the various factors investigated.

WM. B. PLUMMER

Use of bituminous coal as generator fuel in plants of the United Gas Improvement Co. H. K. SEELEY. *Proc. Am. Gas Assoc.* 1924, 777-84.—Operating data are tabulated for 8 U. G. I. plants, covering generators from 5 ft. to 10.5 ft. in diam., coals from 4 different localities, and mixts. of 50-100% coal. The capacity is not seriously reduced for mixts up to 90% coal (7-ft. generators or smaller), 80% (7- to 9 ft.), or 60-75% (over 9-ft. size). In charging coal-coke mixts, the coke should be dumped first and without spreading so as to keep the resistance of the center of the bed low. The use of screened coal must depend on the local price of boiler fuel, as the increase in generator efficiency is not large enough to counterbalance very low credits for the fines removed. Blow-run operation must ordinarily be used for short periods to keep down superheater temps., and may be used to increase the capacity, but if oil is expensive the added cost of long blow runs is such that it would ordinarily be more economical to use a larger % coke to increase the capacity rather than to lengthen the blow run.

WM. B. P.

Tests by different companies (of the use of bituminous coal as generator fuel). ANON. *Proc. Am. Gas Assoc.* 1924, 785-804.—Brief reports of the experiences of 8 companies with the use of bituminous coals, in general the capacity was reduced 10-25% for 100% coal, an increase was reported in one case for an 80/20 mixt. Detailed operating data are given covering the application of the backrun process to bituminous coals.

WM. B. PLUMMER

New Zealand brown coals. Low- and medium-temperature carbonization experiments with typical high-sulfur and low-sulfur coals. J. A. GELMAN AND W. P. EVANS. *J. Soc. Chem. Ind.* 44, 263-4T(1925).—The app. used was the standard form adopted by the Fuel Research Board, with slight modifications. A break in the H curve at about 600° marks the transition from the low- to the high-temp. reactions. Tables of data are given.

H. L. OLIN

New Zealand brown coals, with special reference to their use in gas producers and for low-temperature distillation. W. O. R. GILLING AND W. P. EVANS. *J. Soc. Chem. Ind.* 44, 259-63T(1925).—Extensive producer tests were made on 2 New Zealand brown coals, one fairly good and the other poor. The first produced about 55 cu. ft. of a 135-B.t.u. gas; the second only 43 cu. ft. of 120-B.t.u. Later work was done with 2 producers in series in an effort to eliminate tar from the gas. Data on the calorific values of low-temp. oils from 4 coals are given. A preliminary note on the extrn. of these coals with  $\text{Me}_2\text{CO}$ ,  $\text{C}_2\text{H}_6$ ,  $\text{CS}_2$ ,  $\text{EtOH}$ ,  $\text{Et}_2\text{O}$ , light petroleum, pyridine and  $\text{H}_2\text{O}$  is given.

H. L. OLIN

New Zealand brown coals. Elimination of sulfur during carbonization. W. P. EVANS. *J. Soc. Chem. Ind.* 44, 265T(1925).—A table and graph show the progressive desulfurization of a New Zealand coal on the application of heat. The main elimination depends upon the formation of  $\text{H}_2\text{S}$ , which takes place at a relatively low temp.—below 600°, at which point 70% is removed.

H. L. OLIN

Brown coals of New Zealand. Organic sulfur as a factor in determining the rank of a lignite coal. W. P. EVANS. *J. Soc. Chem. Ind.* 44, 258T(1925).—The scheme of using the C-H ratio for detg. the rank of a coal is inaccurate unless org. S is calcd. as part of the coal substance instead of being eliminated from the computation as is commonly done.

H. L. OLIN

New Zealand brown coals. Some hard jet-like inclusions found in the resin-bearing seams at Coal Creek Flat, Central Otago. W. P. EVANS. *J. Soc. Chem. Ind.* 44, 266T(1925).—Hard, resistant inclusions found in this coal are judged from their ash compn. to be weathered basalt bound by a bituminous cement. In any case they were not derived from the original coal but are drift material from some other bed.

H. L. OLIN

The production cost of powdered brown coal and the limits of its application to

boiler firing. K. DEIMLER. *Braunkohle* 24, 129-36(1925).—With a raw brown coal of 55%  $H_2O$  and a heating value of 2400 kg. cal./kg., drying to 13%  $H_2O$  will increase the latter to 5525, the cost being given as 6.52 m./10,000 kg. original coal, on the assumption of an evapn. of 1.0 lb.  $H_2O$ /1.4 lb. steam and 5% losses. No actual cost data are given for pulverization. An extensive calcd. table is given showing the heating value vs. the %  $H_2O$  for various coals (the range is 4000-7000 kg. cal./kg. at 0%  $H_2O$ , by steps of 100) over the range of 0-70%  $H_2O$ . Another table and diagram similarly show boiler efficiency vs.  $H_2O$  content for various coals. WM. B. PLUMMER

The present aspects of brown coal firing. BERNER *Braunkohle* 24, 80-93, 109-15(1925).—A no. of different types of mechanical and hand-operated grates for firing low-grade fuels are described (cf. preceding abstract). Test data for several types show efficiencies of 80-83% for brown coals of heating value 1900-2800 kg. cal./kg. and 11%  $H_2O$  up to 55%; other data representing the av. performance at 25-33 kg. steam (at 15 atm.)/sq. m./hr., which corresponds to a coal rate of 155-350 kg./sq. m./hr. With hand-operated grates the ratio of grate area to heating surface is  $1/11$  while with mechanical operation it is  $1/11$ . WM. B. PLUMMER

Further occurrence of methane in brown-coal mines. H. FLEISSNER. *Brennstoff-Chem.* 6, 106-8(1925); cf. C. A. 19, 809.—F. disagrees with Erdmann (C. A. 19, 1455) who thinks that methane found in brown-coal mines is of volcanic origin and not a coalification product. Methane occurrence is pretty general in the Austrian fields, particularly where the cover of the beds is thick. Where the cover is thick, methane formed during coalification does not escape so easily as where the cover is thin as in Germany. J. D. DAVIS

Further researches on the various types of pyrites in coal, especially in relation to spontaneous combustion. JAMES LOWAN. *Colliery Guardian* 129, 1317-8(1925).—An illustrated description of the occurrence and characteristics of various types of pyrites. A microscopic study indicates that the different types were formed by different micro-fungi and bacteria, the former first breaking down the cellulose walls of the vegetable structure and then the bacteria decomposing S and Fe compds., which had been absorbed by the plant, to form pyrites. Cryst. pyrites under normal conditions does not oxidize and is harmless, but in a finely divided state it oxidizes easily and may cause spontaneous combustion. Massive pyrites oxidizes rapidly under some conditions and may be classed as a dangerous form. Nodular pyrites is a source of spontaneous combustion when in large masses. Stringy pyrites is harmless under normal conditions. Granular pyrites when associated with coal of the vitrain type does not oxidize and is harmless. Globulitic pyrites oxidizes rapidly and is dangerous when it occurs in soft coal in a partially oxidized form but when fully oxidized in a coal of the durain type, oxidation does not occur. C. C. DAVIS

A new low-temperature carbonization process for coal. The Dohbelstein process. A. THAU. *Fuel in Science and Practice* 4, 259-63(1925).—A dense hard coke is possible only when coal is undisturbed during carbonization and a low carbonization plant is most economical when undisturbed carbonization is carried out with continuous operation. These conditions are fulfilled in the new Dohbelstein process, which has been developed on a semi-com. scale. The oven is a complex horizontal cylinder, the center of which consists of a double tube like the fire tube of a Cornish or Lancashire boiler. This is surrounded by an outer shell or tube in which are fastened at short regular distances circular double-walled cells. Heating gases pass from the inner tube into and through the cells, between which are small chambers for the coal. The whole app. rotates at such a rate that 1 turn corresponds to the coking time of the charge (3-5 hrs.). The complete equipment has further accessory parts, including means for automatic charging and discharging. No dust contaminates the tar, the power consumption is small and the only function of the rotation is for charging and discharging. The capacity is large and the distance between cells is varied according to the % volatile in the coal. Coal contg. 26% volatile has been carbonized with the heating gas entering at 550-660° and issuing at 340-50°. The coke resembles metallurgical coke in structure and in quality lies between gas-coke and metallurgical coke-oven coke, but has a denser structure free from large pores and it forms larger lumps than gas-coke. It still contains about 10% volatile and burns without smoke. C. C. DAVIS

The hydrogenation and liquefaction of coal. II. The hydrogenation and destructive distillation of Arley coal. H. G. SHATWELL and A. R. BOWEN. *Fuel in Science and Practice* 4, 252-5(1925).—Expts. similar to those already published (C. A. 19, 1188, 1767) were carried out on a coking coal of lower C content (Arley). This coal contained in %: C 83.27-85.85, H 4.61-5.70, S 2.39 max., N 1.86 max., volatile 30.1-36.33 and gave a hard, compact coke after both high and low temp. distn. Hydrogenation for

12 hrs. at a max temp of 430° and max pressure of 127 atm. rendered 67.6% of the original ash free dry coal sol. in PhOH and 61.4% sol. in  $\text{CHCl}_3$ . Similar treatment in the presence of N converted only 7.7% to a substance sol. in PhOH. The total H consumed during hydrogenation was 3.76% of the coal; that fixed by the liquid and solid reaction products was 2.31%. The liquid product did not consist entirely of hydrocarbon, but contained appreciable amts. of substances contg. S, N and O. The yield of oil was substantially greater than that from Graigols coal and from a non-coking coal subjected to the same treatment.

The coking and swelling constituents of coal. FRANZ FISCHER. *Ind. Eng. Chem.* 17, 707-11 (1925).—Various coals were extd. with 1320 cc. of  $\text{C}_6\text{H}_6$  for 490 g. pea-sized coal in a mechanically shaken autoclave, heated at 285° for 1 hr. For coals of decreasing geologic age (non-sintering coals down to caking and swelling coals) the % extd. increased from 1.34 to 7.76%, the no. of 1 hr. extns. required from 3 to 8. The coal after extn. is crumbly and without metallic luster, coals originally strongly caking and swelling becoming non-sintering, the original properties are, however, restored on returning the substance extd. (by evapn. of its  $\text{C}_6\text{H}_6$  soln. in contact with the extd. coal). The character of the  $\text{C}_6\text{H}_6$  ext. varies, passing (with decreasing age) from plastic to brittle, its m. p. ("drop point") increases from 43° to 89°. On treatment with petr. ether the ext. is sepd. into a "solid bitumen" and an "oily bitumen". With decreasing age the % solid bitumen in the ext. increases from 29.4 to 49%, the temp. at which it decomposes (with strong gas evolution) decreasing from over 300° to 178°. The oily bitumen is the substance which detrs., mainly by the amt. thercol present, the temp. of the plastic state during coking, and also the final degree of caking; if the decomposition of the solid bitumen comes within the plastic range of the coal a swollen and porous coke is formed. Given further data on other coals, the quantities and properties of the oily and solid bitumens as above described should give an accurate index of coking properties.

Burning raw coal on step grates. FRADEL. *Feuerungstechnik* 13, 213-3 (1925); cf. following abstr.—P. describes and illustrates a new form of grate made up of small rectangular elements, half oscillating and half stationary, arranged like a checker-board. This prevents the uncovering of any part of the grate. ERNEST W. THURLE.

The "caterpillar" grate for low-grade fuels. FRADEL. *Braunkohle* 24, 73-8 (1925), cf. preceding abstr.—The grate units consist of axial segments of a cylindrical surface, pivoted at the bottom to rockers in groups of 6 per rocker, the segments being placed concave downwards with their free side resting on top of the next lower segment. The grate surface slopes downwards at about 20°. The rockers are mechanically operated to produce a constant undulatory motion (forward) of the grate surface. Test data are given for a no. of low grade fuels, for a brown coal contg. 51.8%  $\text{H}_2\text{O}$ , 6.73% ash, 2160 kg. cal./kg. the grate has a capacity of 321.6 kg. coal or 697,550 kg. cal./sq. m./hr. at a boiler efficiency of 65-80%.

The distillation of certain French lignites. A. MAHLE. *J. mines gas* 49, 163-6 (1925).—A lignite from the Caunette seam (Hérault) contg. very little  $\text{H}_2\text{O}$  (3-7%) was distd. in 200 g. quantities in a current of steam at temps. increasing from 200 to 500°, the tar being fractionally collected. The temp. of max. tar formation is approx. 380°. Repetitions of such runs gave enough of the tar formed in each of the several temp. ranges to permit its examn. The following figures represent, resp., the av. temp. of formation, the % distd. at 300°, the % distd. to pitch at 380°: 200, 35, 95; 345, 51, 88, 380, 26.5, 61, 430, 28.5, 65, 475, 25, 67. The phenols from a com. tar from this lignite are largely cresols and xylenols, b. p. data for the neutral oils are also given.

The composition of peat and the lignin theory. J. MARCUSSEN. *2. angew. Chem.* 38, 339-41 (1925).—On refluxing 10 g. of peat with 200 cc. of 1% NaOH for 2 hrs. 50% (on the peat) of humic acid (I) is ptg. with the filtrate by dil.  $\text{H}_2\text{SO}_4$ , after which by addn. of a slight excess of NaOH, evapn., Lht. extn. with 50% alc. there is obtained 30% of humic acid (II). Similar treatment of oxycellulose (III) gives the same product II. Since the cellulose content of peat is only 7-15% while the total polysaccharides are approx. 37%, the similar behavior of peat and III in forming II seems to prove definitely that peat contains large amts. of III. Further confirmation is given by the fact that similar  $\text{H}_2\text{O}$  sol. acids are formed by long boiling of peat or III with  $\text{H}_2\text{O}$ . The pure II contains 43% C, 6% H, and 51% O, reduces Fehling soln. and gives a blood-red color with  $\text{FeCl}_3$  and NaOH, its equiv. wt. being 350, its phenylhydrazone m. 168°. II forms I on evapn. of its aq. soln. contg. dil. HCl or  $(\text{CO}_2\text{H})_2$ , which in conjunction with the absence of lignins from certain peats indicates that I is formed from III via II, instead of from lignins as generally accepted.

WM. B. FLETCHER

Hydrogenation by the Bergius process. H. G. SHATWELL. *Chemistry & Industry* 44, 471-7(1925).—In the Bergius process hydrogenation is accomplished by heating the raw material to 400-50° with H under 1-200 atms. Coal or asphalt so treated yields oils; paraffin wax and heavy oils yield lighter fractions.

Gasification tests of cottonseed. ROGER MARTIN. *Chaleur et industrie* 6, 195-9 (1925).—Complete results of a test are given and commented.

Commercial manufacture of synthetic alcohol. F. VALLETTE. *Chimie et industrie* 13, 718-21(1925).—Description of the process to be used shortly at the Béthune mines for the manuf. of EtOH from the  $C_2H_4$  of coke-oven gases. The gases are compressed and cooled (for sepn. of H for the manuf. of synthetic  $NH_3$  by the Claude process) in such a manner that the various gases ( $C_2H_4$ ,  $C_2H_6$ ,  $CH_4$ , CO, etc.) are obtained separately. The  $C_2H_4$  is absorbed continuously in  $H_2SO_4$  contg. about 18%  $C_2H_4$ , which is agitated and kept at 40-50°. The resultant  $EtHSO_4$  is fed to the distg. column (without previous diln.) where it circulates in counter current to steam and  $NH_3$ , the upper sections of the column acting as dephlegmator. The  $NH_3$  accelerates the sapon by increasing the temp. and by combining with the  $H_2SO_4$ . A 30-60% crude alc. is obtained, according to the height of the column, and the  $(NH_4)_2SO_4$  is sold as fertilizer. The cost of production is discussed, it compares favorably with that of distillery alc.

A. PAPINEAU-COUTURE

Synthetic methanol. R. T. LAWORTH. *Can. Chem. Mfr.* 9, 139-40(1925).—A résumé of the Badische (cf. C. A. 18, 459, 4705), Patart and Audibert processes for prepg. MeOH from water gas and H, with a short bibliography. The first process mentioned employs purified water gas contg. 60% H, 30% CO, together with  $CO_2$  and N, at 200 atm. pressure, over a catalyst maintained at about 400°. Catalysts are mixts. of metal oxides belonging to different groups in the periodic system, as 90 parts ZnO and 10 parts  $Cr_2O_3$ ; 85 parts ZnO and 15 parts V oxide, or 90 parts CdO and 10 parts  $Cr_2O_3$ . Gases used must be purified carefully, particularly for S and volatile Fe compds. The Merseberg plant produces about 10 to 20 tons per day at 20¢ per gal. The Patart process (cf. Lormand, C. A. 19, 2027) uses as catalyst 90% CuO and 10% ZnO at temps. of 400-420° and at pressures of 150 to 250 atm. It gives a product at 22 to 32¢ per gal. Audibert uses catalysts contg. suboxides of V, Mn, W, Pb and Bi. The economic importance of these processes is emphasized.

W. C. EBAUGH

The calculation of flue gas analysis from the carbon dioxide and oxygen content. H. KOLBE. *Braunkohle* 24, 209-18(1925).—Formulas for the calcn. of the % combustible in the gas, and for the detn. of heat balances, are derived and discussed, 3 tables are included.

WM. B. PLUMMER

Gummy deposits in gas meters—causes and prevention. R. L. BROWN. *Proc. Am. Gas Assoc.* 1924, 1353-1411; cf. C. A. 19, 880.—A complete report with assembled data. Complete analyses are given for 5 light oils, including total unsatn. and styrene and indene content; full analytical data are also given for a no. of drip oils, and various samples of the gummy deposits proper. The relation of plant operation, O content of the gas, and unsatd. hydrocarbons in the gas to gum formation is discussed in detail.

WM. B. PLUMMER

Report of the purification committee. A. F. KUNBERGER. *Proc. Am. Gas Assoc.* 1924, 1412-26.—Various points concerning the operation of ordinary purifier boxes are emphasized. Boxes passing 80% of the S at a gas temp. of 60° F. passed only 25% when the temp. was raised to 90° F., the higher temp. also being advantageous in preventing the condensation of  $H_2O$ . An active oxide (fouling test, 65% on 4 foulings) at a cost of 1 cent/lb., as compared to a less active one (35% on 4 foulings) at 0.5 cent/lb., may reduce purification costs by 30%. Tabulated data are given for 9 European plants using oxide without shavings, the pressure drops across the boxes not being excessive, the efficiency being apparently good, the advantages being obvious. The condensed answers to a general questionnaire on purification sent to various plants are given.

WM. B. PLUMMER

Reports submitted by manufacturers of carbonizing apparatus. ANON. *Proc. Am. Gas Assoc.* 1924, 1139-91.—Isbell-Porter Co. A description, with plant lay-outs of 2 Woodall-Duckham installations under construction at Roanoke (Va.) and Buffalo (N. Y.). Koppers Co. The Becker type small gas oven and its auxiliary equipment and operation are described; 7 installations, operating or under construction, are listed. Of the full size Becker type ovens 9 installations are operating (total 796 ovens) and 5 more are under construction. Parker-Russell Mining and Mfg. Co. A narrow gas oven installation (Kalamazoo, Mich.), a new charging and discharging machine for gas retorts, and a design for vertical gas ovens are described. Russell Engineering Co. A 2-ton horizontal oven plant operating at Quincy (Ill.), and a new arrangement of scrubber

A muffler for water-gas blower inlets. ROBERT LINDSAY. *Proc. Am. Gas Assoc.* 1924, 886-7.—Because of local complaints concerning the noise made by the blowers all which were muffled, for example a No. 10 Sturtevant by means of a wooden box 12 X 8 X 8 ft. with 4 baffles, and larger for other larger blowers. WM. B. PLUMMER

Report of the Bartlett Hayward Co., Baltimore, Md. H. I. UNDERHILL. *Proc. Am. Gas Assoc.* 1924, 877-9.—Describing a waste-heat boiler of their construction, which with standard 12-ft. diam. carburetted water gas sets gives a steam production of 45-50 lbs./1000 cu. ft. gas. WM. B. PLUMMER

The Kennedy automatic control for water-gas sets. ANON. *Proc. Am. Gas Assoc.* 1924, 880-1.—The app., constructed by the Bartlett Hayward Co., is of the elec. type and is provided with interlocking safety devices, can be readily adjusted during operation, and may be provided with an automatic carburetor blast creeper or device for mechanically increasing the secondary air supply. WM. B. PLUMMER

A high-speed conveyor charging belt for charging Williamson generators at the Nassau Plant of the Brooklyn Union Gas Co., Brooklyn, N. Y. ANON. *Proc. Am. Gas Assoc.* 1924, 882-3.—Difficulty in charging coke from the 6-ton larry to the generators, due to its sticking in the chutes, led to the installation of a 16-in., 1200-ft./min. belt conveyor, requiring 5 b. p. and easily movable within the distances involved. WM. B. PLUMMER

Water gas apparatus developments from the Western Gas Construction Co., T. W. STONE. *Proc. Am. Gas Assoc.* 1924, 856-67.—The following are described with photographs: a special dome-top construction, an angle-connected reversing valve operating with 1 disk for both sides, a water-cooled oil spray, a hydraulic safety block, waste-heat boilers, and miscellaneous charging equipment. WM. B. PLUMMER

The Western automatic control for water-gas sets. ANON. *Proc. Am. Gas Assoc.* 1924, 868-9.—A hydraulically operated automatic control is described. The whole cycle can be altered in const. ratio, or any part of it can be changed at will, without interruption of the action of the automatic control. WM. B. PLUMMER

Report of the U. G. I. Contracting Co., Philadelphia, Pa. C. J. O'DONNELL. *Proc. Am. Gas Assoc.* 1924, 871-7.—An installation for the Rochester Gas and Electric Corp. of a 12-ft. U. G. I. cone-top, hopper-bottom set, of capacity 4,500 M cu. ft./24 hrs. is described. Special features consist of the use of a steam accumulator, high-pressure oil feed with a checkerless carburetor, and a 42-in. Haug combined valve and producer gas-blast mixer at the entrance to the carburetor. The U. G. I. automatic water-gas control is also described. WM. B. PLUMMER

Report of the uncarburetted-water-gas section. J. H. WARRICK. *Proc. Am. Gas Assoc.* 1924, 837-47; see C. A. 19, 885. WM. B. PLUMMER

Water-gas apparatus from the Gas Machinery Co., Cleveland, Ohio. W. E. STEIN-WEDELL. *Proc. Am. Gas Assoc.* 1924, 851-5.—Photographs and a very brief discussion of some of their app., particularly for automatic control of water-gas sets. WM. B. PLUMMER

Refractories (for water-gas sets). W. M. RUSSELL. *Proc. Am. Gas Assoc.* 1924, 822-9.—Crowns have been successfully cast in place on water-gas generators, with suitable wooden forms and a mixt. of 10% Johns-Manville No. 3200, 8% anhyd. Na silicate, and 82% fire clay; after 6 months service such a crown in a 6.5-ft. generator had not even checked. A carborundum lining for an 11-ft. generator has been in use by the Binghamton Gas Works since Oct. 1922 with a net saving due to decreased clinker troubles. The use of blocks about 0.5 the size of the usual fire-brick shapes has prevented trouble due to expansion and cracking, no trouble having been encountered due to expansion and cracking, no trouble having been encountered due to oxidation, probably because their fuel is a good grade of anthracite with very low Fe. A diagram shows the construction of the lining in detail. *Bernitz blocks* have been in test and use by the Gloucester Gas Light Co. since May 1922. These consist of hollow, inter-connecting shapes, with perforated inner walls, part of the blast (and reversibly the steam) passing through the blocks and into the fuel bed through these perforations. The cooling and mechanical action of the blast prevent adherence of clinker to the walls. These blocks are ordinarily carried to a height of 36-40 in. above the grate bars. For most purposes Mutton Hollow silica is satisfactory as a material, but for badly clinkering fuels carborundum has been used for making the blocks; no trouble has been experienced with their cracking or oxidation. Diagrams show in detail the construction of the linings. WM. B. PLUMMER

The illuminating gas industry in Germany and fuel economy. F. MUHLERT. *Chaleur et industrie* 6, 167-72(1925).—Description of present conditions. A. P.-C.

Gas-works coke ovens and the utilization of coke fines in gas producers. CH.

BERTHELOT. *Chaleur et industrie* 6, 131-5, 189-93(1925).—A discussion of the merits of the use of mixed gases for heating the ovens and of coke fines in the producers, giving results obtained in the gas works at Vienna (Austria) and Mannheim-Luzenberg.

A. PAPINEAU-COUTURE

Present-day tendencies in the selection of gas producers. PIERRE APPELL, *Chaleur et industrie* 6, 200-1(1925).—Brief discussion of the relative merits of rectangular and round producers. The chief advantage of the latter is the possibility of using a rotating grate which eliminates the necessity of hand stoking. The Sauvageot grate, with hollow rotating bars, allows of automatic stoking with rectangular producers.

A. PAPINEAU-COUTURE

Furnace heating. IV and V. R. J. SARIANT. *Fuel in Science and Practice* 4, 199-208(1925), cf. *C. A.* 19, 2120.—A discussion of the flow of gases in furnaces, chiefly from the mathematical point of view, the design of metallurgical furnaces with regard to the draft, the velocity and friction loss in flues, the buoyancy factor, fuel economy and its control, the utilization of waste heat, waste-heat boilers, heat insulation and recuperation. The text is illustrated with photographs and diagrams. C. C. DAVIS

Report of the Lynn Gas and Electric Co. F. E. DRAKE, *Proc. Am. Gas Assoc.* 1924, 889.—An automatic device for purging the carburetor oil spray nozzle with steam at the end of the make run is described. "H" beams are more satisfactory than "I" beams as generator grate supports, as their wider flanges hold more protective refractory material.

WM. B. PLUMMER

The question of decomposition of primary tar and light oils in rotary low temperature retorts. F. HOFFMANN. *Brennstoff-Chem.* 6, 85(1925).—H thinks that the double-cylinder retort recommended by F. Muller (*C. A.* 19, 719) will not minimize cracking of primary tars since this design has as much heating surface with which the vapors may come in contact as the old single-cylinder retort.

J. D. DAVIS

A new process of coal tar distillation. A. TITAU. *Glückauf* 61, 369-71(1925).—A new furnace construction by O. Debelstein, permitting a continuous distn. of the coal in rest, is described.

OSCAR PAUK

Extraction of phenols from tar oils by the caustic soda process. J. J. MORGAN AND M. H. MEIGHAN. *Ind. Eng. Chem.* 17, 696-700(1925).—A review of various processes for obtaining phenol and cresols from tar oils shows that the concn. of the solns of NaOH employed for the purpose varies within wide limits in different factories. Sets of expts. were made on Hydrogas tar oil (a Doherty Hydrogas product including distillates up to 365°) and coke oven tar oil (a high temp. tar oil), by extg. them with NaOH solns. varying from 4.8 to 49.6%. For hydrogas oil a max. extn. is obtained with a soln. contg. 23.5% NaOH; for coke oven tar oil complete extn. is had with solns. contg. over 19% NaOH. A study must be made on each tar to determine conditions for extn. with NaOH. It is possible to make a partial sepn. of phenols by varying the amt. of caustic used in extg. the oil. Furthermore, by suitable control it is possible to ext. from the tar oils phenols of any av. mol. wt.

W. C. EBAUGH

Coöperative analyses and tests of light oils and tars. J. M. WEISS. *Proc. Am. Gas Assoc.* 1924, 1334-43.—A revision, correction, and enlargement of Chapter 2, Parts 3 and 4 of the Gas Chemist's Handbook. A new metal flask and glass column and condenser are described for the fractional distn. of light oil. Tests are given for the sulfonation residue of light oil and the solidifying point of pure benzene. Adoption of the A. S. T. M. test D95-23T for water in bituminous materials is recommended. In the pitch m. p. (in air) test, the use of a large shield completely surrounding the oven and burner is specified. In the float test for road tars, adoption of the A. S. T. M. test D139-23T is recommended. Methods for the crude  $C_{12}H_{10}$  detn., consistency of distn. residue, and coke test for middle and heavy oils are given.

WM. B. PLUMMER

The investigation and refining of brown-coal tar. WILHELM FRANCKENSTEIN. *Z. angew. Chem.* 37, 878-82(1924).—A brown-coal tar of  $d_{20}^{20}$  1.024 and  $C_{12}H_{10}$ -insol. 5.61% was studied. All % figures following refer to the original dry tar. Vacuum distn. to a vapor temp. of 325° gave 64.5% of distillate of  $d$  0.935 and 33% tar acids, the 33% of pitch which remained giving on cracking distn. at atm. pressure 19.8% of a distillate of  $d$  0.855 and 6% tar acids. The combined distillates had a  $d$  of 0.913 and 23% tar acids, and yielded 10.3% crude paraffin, after removal of which steam distn. gave 31.9% heavy oil (suitable for lubricants after NaOH washing) and 41.7% of light oil, which after NaOH washing shrank to 30.6%. Steam distn. of the original tar (up to 210°) gave 36.9% of distillate, the asphaltic substances being sepd. from the residue by its partial soln. in  $C_{12}H_{10}$ , and the asphalt-free oils refined and sepd. Complete refining data are given.

WM. B. PLUMMER

A water-gas tar filtration system. R. S. CARTER *Proc Am Gas Assoc.* 1924, 1427-31; cf. *C. A.* 19, 1459.—A brief description of plant and results using centrifugal and pressure-spray dehydration methods. WM. B. PLUMMER

Other waste emulsions incidental to manufactured gas production. G. A. SIMMONS. *Proc. Am. Gas Assoc.* 1924, 1431-8.—Tar contg 25%  $H_2O$  is indirectly heated by steam to 215° F., the heat economy being such as to make the total (labor + steam) cost approx 0.3-0.4 cent/gal dry tar. WM. B. PLUMMER

Coke yields by high- and low-temperature carbonization. F. W. SPERR, JR. *Ind. Eng. Chem.* 17, 763-4 (1925).—The figures given by Morrell and Egloff (*C. A.* 19, 1770) for tar yield and gas B. t. u. for high temp. carbonization represent British practice (and units), tar yields for modern American coke ovens being 10-11 gals./ton, the gas being about 550 B. t. u. J. C. MORRELL AND GUSTAV EGLOFF *Ibid* 764.—M. and E. agree that their figures do not represent American coke-oven practice, but show that the ratio of tar yields for low temp. high temp. carbonization, which was the point they desired to bring out, is 2.36 for their tabulation (Tupholme's data) and is 2.37 using Sperr's data with those of Morgan and Soule (*C. A.* 16, 2591). The same applies to the gas B. t. u., their ratio for low high temp. carbonization being 1.61 whereas Portier gives 1.54. WM. B. PLUMMER

An automatic apparatus for the determination of water in coals, tars and oils. KURT SCHAEFER. *Chem.-Ztg.* 48, 761 (1924).—The app. uses the common principle of reflux distn. with xylene, the  $H_2O$  being tapped in a small graduated container from which the xylene overflows and returns to the boiling flask. WM. B. PLUMMER

Improving the quality of coke products in horizontal retorts. JOHN H. DOERRES, JOHN L. EIGENBROT AND R. L. FLETCHER *Proc Am Gas Assoc.* 1924, 974-80; cf. *C. A.* 19, 886.—Tests were made in several coke-oven and horizontal retort plants on the same mixts. of 10-15% low-volatile (New River) coal with 90-85% of high volatile (Westmoreland or Elkhorn) coal. No fixed rule expresses the relation of coke density to the admixture of low-volatile coal, but the size and strength of the coke are generally increased. The full effect of this admixing in coke ovens cannot be obtained without pulverization of the fuel, which point requires further study. Tables and photographs are given. WM. B. PLUMMER

By-product coke-oven practice. V and VI. R. A. MORR *Fuel in Science and Practice* 4, 185-93 (1925).—In continuation of a general survey (cf. *C. A.* 19, 2122) the development and operation of the Smet-Solvay and Coppée ovens are described and illustrated.

Bituminous emulsion [for briquets of coal] (U. S. pat. 1,542,626) 22.

Plant for generating fuel gas from oil. W. E. BAKER U. S. 1,542,738, June 16.

Coal feeder for gas producers. C. A. SCHRANZ U. S. 1,542,732, June 16.

Thermostatic control for oil burners. W. E. SHORE U. S. 1,543,127, June 23.

Coke-oven gas-main valve. H. KOPPEKS U. S. 1,542,065, June 16.

## 22—PETROLEUM, LUBRICANTS, ASPHALT AND WOOD PRODUCTS

F. M. ROGERS

Chemistry of petroleum. I. Occurrence of compounds of sulfur in the light distillate from the crude oil of Maidan-i-Naftun (Persia). S. F. BIRCH AND W. S. G. P. NORMAN. *J. Chem. Soc.* 127, 898-907 (1925).—After being kept for some time at atm. pressure, the crude petroleum retains very little  $H_2S$ , and has a "faint, somewhat sweet odor." The S compds. in the distillates (from the 36% by vol. of the crude that yields the com. naphtha and burning oils) have highly objectionable odors. This difference between the crude and the distillates is regarded as proof that the S compds. of the distillates are not present in the crude petroleum but are formed by decompn. of other substances during distn. Elementary S appears when the crude reaches 120°, and the amt. of free and combined S in the earlier distillates is reduced by using much steam, thereby keeping the temp. low. The S compds. identified were sepd. from "spent soda" (the used soln. of NaOH with which the distillate was treated in the refinery). From 40 gal. of clear spent-soda, 720 cc. of S compds. was obtained by distn. In order to sep. the acidic from the non acidic compds., the distillate was shaken with a 50% soln. of KOH. The insol. non acidic portion was sepd. mechanically from the alk.

soln., while the acidic constituents were liberated by neutralizing the soln. with  $H_2SO_4$  (temp kept below  $30^\circ$ ). The oil that sepd. (350 cc.) was distd. with steam, and dried with  $CaCl_2$ . The dried oil was distd. fractionally through a 24" Hempel column into 5° fractions. On redistn., a graph was plotted, showing vol. of fraction vs. final b. p. of fraction. Pronounced peaks at  $57.5^\circ$  and  $88.0^\circ$  showed presence of isopropyl and isobutyl mercaptans. About 18% of the total was collected between  $36^\circ$  and  $50^\circ$ , it was apparently largely  $EtHS$ , but the small vol. of it made sepn. by further distn. impractical. Further distn. of the other fractions yielded relatively pure products. The mercaptans were identified further by analysis and by the study of derivs.: mercurichlorides, disulfides, and Ba sulfonates. The non-acidic portion was washed with  $H_2O$ , dried over  $CaCl_2$ , and distd. fractionally with a 6" Hempel column (10° fractions first time, then 3° fractions). After 2 distns., a graph indicated the presence of diethyl disulfide, diisopropyl disulfide and diisobutyl disulfide. These compds. were identified by converting them to the mercaptans and making derivs. of the products. The Na mercaptides are hydrolyzed during distn. of the spent soda, but  $Na_2S$  or Na polysulfides are not hydrolyzed. The mercaptans distil or are converted into disulfides by the oxidizing action of  $NaOH$  and Na polysulfides.

W. F. FARAGHER

Some crude Russian petroleum from the Caspian Sea oil fields. P. M. E. SCHMITZ. *Mat. grasses* 17, 7210-1(1925).—Crude petroleum from Binagady (near Baku) had  $d_{15}$  0.9118, flash point (open cup)  $54^\circ$ , asphalt 28%. Distn. in an Engler flask with Glinisky 3 bulb distg. column gave: to  $140^\circ$  4.41%;  $140-50^\circ$  1.95%;  $150-270^\circ$  17.82% ( $d_{15}$  0.8356, Abel Pensky flash point  $36^\circ$ );  $270-80^\circ$  3.88%;  $280-90^\circ$  1.84%; residue 69.9% ( $d_{15}$  0.9518, flash point in open cup  $164^\circ$ , asphalt 64%); losses 0.20%. Crude petroleum from Swjätini Island had  $d_{15}$  0.9212, flash point (open cup)  $62^\circ$ . Distn. in an Engler flask without distg. column gave: to  $125^\circ$  0.31%;  $125-270^\circ$  16.8% ( $d_{15}$  0.8217, A.P. flash point  $17.5^\circ$ );  $270-85^\circ$  3.53% ( $d_{15}$  0.8646, flash point  $21.5^\circ$ ); residue 78.92% ( $d_{15}$  0.946, flash point (open cup)  $170^\circ$ , Engler viscosity at  $100^\circ$  2.93, asphalt 56%). Distn. in an Engler flask with a 3-bulb Glinisky distg. column of a crude having  $d_{15}$  0.9243, flash point (open cup)  $78^\circ$ , asphalt 60%, gave: to  $140^\circ$  2.53%;  $140-50^\circ$  0.51%;  $150-270^\circ$  12.68% ( $d_{15}$  0.8353);  $270-80^\circ$  1.96%;  $280-90^\circ$  2.60%; residue 79.53% ( $d_{15}$  0.9491, flash point (open cup)  $168^\circ$ , asphalt 76%). Distn. of this crude petroleum with superheated steam gives 25-30% of white-colored products, 45-50% of low-grade lubricating oils, and 18-22% of high-grade asphalt. Com. distn. of Emba (north of the Caspian Sea) crude gave: crude gasoline 6 (d. 0.760), kerosene 20, gas oil 7, lubricating oils 24, tar 29 (d. 0.910, flash point (open cup)  $280^\circ$ ), losses 4%. Com. distn. of a Tchélékén crude having d. 0.879 gave: gasoline 9, kerosene 26, paraffin oils 33 ( $d_{15}$  0.965-0.870, Engler viscosity at  $60^\circ$  1.30, solidifying point  $28^\circ$ ), tar 27, losses 5%. The crude contains about 5% of paraffin, of which 3-4 is recovered commercially. It can be used also for the production of vaseline, the yields being 40-50% of brownish yellow, technical grade, or about 20% of white medicinal grade. The paraffin and vaseline from Tchélékén crude are equal to the best American products.

A. PAPINEAU-COUTURE

Oil shale and its utilization. H. TRÜNKLER. *Feuerungstechnik* 13, 205-8(1925).—After a review of other processes, T. sketches briefly his own process for treating poor shales. The residue after distn. is burned on a grate. The gases (with little excess air) are cooled by the introduction of water and passed through the charge to distil it. The non-condensable gases from the distn. are not recovered. Shales contg. down to 4% water may be treated with profit.

ERNEST W. THIELE

Refining Scotland's crude shale oil. E. C. ISOM. *Oil & Gas J.* 24, No. 1, 70, 78 (1925).—The av. yields from crude Scottish shale oil are: motor spirit (gasoline), 12.5%; burning oils (all grades), 23%; gas oil, 17%; lubricating oils, 10.5%; paraffin wax, 9.0%; shale resin, 0.5%; coke, 2.5%; and loss, 25%. The methods practiced in Scotland for refining the product are described.

D. F. BROWN

Electrical dehydration of cut-oil. F. D. MAHONE. *Trans. Am. Inst. Mining Met. Eng.* 70, 1100-4(1924).—The Standard Cottrell, National, and H. F. treaters are described briefly. Statements about the extent of the use of them are included.

W. F. FARAGHER

Formation of oil-field emulsions. D. B. DOW. *Bur. of Mines, Repts. of Investigations* No. 2683, 9 pp. (Mar., 1925).—The formation of emulsions by the flow at high velocities through flow-nipples, leaking valves, and constricted lines, is discussed. It is improbable that cut-oil is produced in the sand, except where the fluid issues from the sand into the well.

W. F. FARAGHER

Centrifuging petroleum-refinery emulsions. E. E. AYRES, JR. *Trans. Am. Inst. Mining Met. Eng.* 70, 1122-30(1924).—If reagents have been used in the field, an addn. of reagents to bottom settlings before centrifuging is not beneficial. If inorg.

matter is less than 2%, the bottom settlings is centrifuged directly. Otherwise, it is agitated with a soln. of  $\text{Na}_2\text{CO}_3$ ,  $\text{NaOH}$ , or water-glass, heated, and settled before it is centrifuged. The most efficient reagent used by A. is Na rosin soap contg. not less than 60% dry matter. It is sol. in oil. Aq. solns. of rosin soap are no better than those of other soaps. After treatment, the rosin soap is present largely in the sep'd  $\text{H}_2\text{O}$ . The oil soln. of rosin soap insures that the soap will reach the droplets of  $\text{H}_2\text{O}$  through the continuous oil phase. Aq. solns. of starch, glue, etc. are as effective as solns. of soaps, especially if a trace of  $\text{NaOH}$  is added. The starch soln. is also useful in removing acidity of sour oils by centrifuging. W. F. FARAGHER

Sinclair's Marcus Hook plant. L. M. FANNING. *Oil & Gas J.* 24, No. 1, 171 (1925).—Description of the plant. D. F. BROWN

Preventable waste in oil refineries. G. EFRS. *Oil Trade* 16, No. 8, 35, 67(1925). D. F. BROWN

Evaporation loss from storage tanks saved with gas balloons. W. K. HALBERT. *Nat. Petr. News* 17, No. 22, 21-3(1925).—By connecting the breathing vents of gas-tight gasoline storage tanks with a balloon made of cotton fabric impregnated with a patented treatment of glue and glycerol to render it gas tight, a reduction in evapn. loss of 0.21% was effected. This amounts to about 6900 gal. per tank per month for the summer months. The impregnated balloon fabric is resistant to oil but not to water and so must be sheltered from the weather. D. F. BROWN

The uses of petroleum with special reference to the production of power. H. BARRINGER. *J. Inst. Petroleum Tech* 11, 104-23(1925).—The discussion is directed particularly to different types of Diesel engine and the performance of various Diesel motor fuels therein. D. F. BROWN

The necessity of the coordinated development of the German mineral oil industry. FABER. *Braunkohle* 24, 149-54(1925).—A plea for coöperation and coördination in the utilization of present resources and the development of new ones. W. B. P.

Boundary lubrication—plane surfaces and the limitations of Amonton's law. WM. HARDY AND IDA BIRCHUMSHAW. *Proc. Roy. Soc. (London)* 108A, 1-28(1925).—When the face of the slider (cf. C. A. 17, 2641, 3602) is plane, the results are strikingly different from those obtained with a slider having a spherical face. With the spherical slider just placed in position, the friction falls to its steady value, but when the slider is plane the friction rises during the "latent period" and the steady value finally obtained is slightly different from the former case. When the steady value is reached, Amonton's law is obeyed. It is found that the rising friction is due to the squeezing out of the lubricant and that the coeff. of friction is really falling, so that if the coeff. of friction  $\mu$  is plotted against the pressure, the curve falls during the latent period to a steady value. This steady value is due not to capillarity but to the operation of the elastic forces between the atoms. The spherical slider corresponds to a vastly increased pressure giving a continuation of the curve. In the latent period there is a coeff. of temp., but beyond this latent period the friction is independent of the temp. With acids, alcohols, and hydrocarbons with a spherical slider, the coeff. of friction is independent of the quantity of lubricant within wide limits starting with the primary film deposited from the sat'd. vapor of the lubricant. Primary films show the squeezing out of the latent period; hence they must be of more than monomolecular thickness, but no pressure used on a plane slider has been sufficient to reduce the coeff. of friction to that of the spherical slider. The coeff. of friction in boundary lubrication is a measure of the efficiency of a lubricant with respect to one variable, i. e., the pressure. This efficiency increases as the layer of lubricant thins out until it becomes const., when some limiting layer is reached. The high efficiency reached in lubrication is due to the orientation of the mols., which occurs even when the layer of lubricant is several mols. deep. This oriented layer is plastic in that it can bear a finite shearing stress without slip. In the latent period adding pressure lowers  $\mu$  and decreasing the pressure raises it but the equil. is not reached at the same rate from the two directions on account of the higher apparent viscosity in the former case due to orientation of the mols. A formula is given for the time of fall of a spherical surface through a liquid and approaching a plane surface as well as for the fall of a flat disk. The time of complete fall is infinite in either case but infinity of a higher order in the latter case. This explains why the spherical slider cuts through the lubricant at once and shows no latent period except that required for the orientation of the mols. Beyond the latent period, after the mols. are oriented, variations in load are not followed by a latent period, for the operation of the elastic forces between the mols. is instantaneous. When plane surfaces have seized, only lubricants which have a sensible vapor pressure will set the faces free, which may mean that only the vapor phase can penetrate. With solid lubricants  $\mu$

is at first too low but becomes normal after the slider has been moved back and forth to disturb mechanically the solid layer. This is not a latent period because time alone will not bring the normal value. There is therefore a natural plane of cleavage in solid lubricants just as in those which are liquid. EUGENE C. BINGHAM

**Stopcock lubrication and an improved lubricant.** E. G. R. ARDAGH AND A. L. DAVIDSON. *Can. Chem. Met.* 9, 137 (1925).—An improvement on "Travers formula" is recommended. Melt 77.5% white petrolatum and 15% white paraffin (m. p. 53°), in a beaker suspended in an oil bath at 130°, and add gradually 7.5% of pale rubber crepe cut into small shreds. Stir continuously for 6 hrs. While still just fluid pour the mixt. in a thin stream on to a cold, clean Al plate, from which it is scraped off and transferred to screw top salve boxes. The lubricant holds a vacuum perfectly, has no appreciable vapor pressure at room temp., shows no tendency to peel, remains effective even when 15% NaOH soln. is allowed to evaporate on a stopcock smeared with it, and retains its elasticity. W. C. ERAUGH

**Studies in lubricating oils.** W. J. WILSON AND B. P. ALLIBONE. *J. Inst. Petr. Tech.* 11, 177-90 (1925).—Methods of evaluating lubricating oils with the results of investigations of the lubricating oil constituents of some crude oils. D. F. BROWN

**The use of coal-tar lubricating oil in mining.** G. BAUM. *Glückauf* 61, 305-9 (1925). OSCAR PAUK

**Charcoal as a gasoline substitute.** Modern processes of manufacture in the woods. A. MAGNEIN. *Technique moderne* 17, 364-7 (1925).—Brief description of the Delhommeau, Magnein, Barbier-Aube, Deperrons, Frey, Laurent and Ringelmann portable carbonization ovens. A. PAFINEAU COUTURE

### Hydrogenation by the Bergius process (SHATWELL) 21.

**Fuel-oil combustion.** W. F. RAYNER. U. S. 1,542,171, June 10. Unvaporized oil particles are directed onto the surface of a liquid material the b. p. of which is higher than the flame temp., e. g., molten Pb. The surface of this material may carry a powdered catalytic agent such as Fe filings.

**Oil-cracking apparatus.** J. G. DAVIDSON. U. S. 1,541,905, June 16. Small resistors within a cracking still are supplied with a c. and, as cracking proceeds, more massive resistors are formed by deposition of C.

**"Artificial turpentine."** J. B. ILLAS. U. S. 1,543,570, June 23. Refined petroleum is treated with  $\text{CaCl}_2$  and alkali, e. g., KOH, and  $\text{H}_2\text{O}$  acidulated with HCl are added and, after standing, the petroleum is drawn off and filtered. These operations are repeated twice and pine oil is added before the final filtration. The product is suitable for use as a drier.

**Apparatus for distilling hydrocarbon oils.** M. F. DEBAJLIETHY. U. S. 1,542,864, June 23.

**Bituminous emulsion.** L. KIRSCHBAUM. *Can.* 247,469, Mar. 10, 1925. An emulsion consists of sulfite liquor, an earthy colloidal material and bitumen, the bitumen being in the dispersed phase.

**Bituminous emulsion.** H. A. MACKAY. U. S. 1,542,626, June 16. See *Brit.* 202,021 (*C. A.* 18, 326).

**Dispersing asphaltic or similar bituminous substances in water.** M. R. CONE. U. S. 1,542,035, June 16. Mech. features.

## 23—CELLULOSE AND PAPER

CARLETON E. CURRAN

**The swelling and dispersion of cellulose nitrate in ethyl alcohol.** KATSUMOTO ATSUKI. *J. Faculty Eng. Tokyo Imp. Univ.* 16, 111-6 (1925).—Nitrates of cotton, wood sulfite and bamboo soda celluloses were treated with 99.2% and 99.8% EtOH and the swelling, gelatinization and peptization of the fibers noted by photomicrographs. Cotton fibers show a swelling of 5-10 times the original diam. in the cell walls with no change in the size of the canal. Surface irregularities appear in the swelled nitrated fiber, this is due to the presence of cuticular tissue. With wood fiber nitrates the tracheids show greater swelling in the pitted portions than in the unpitted parts. The walls of the nitrated bamboo fibers swell and split into consecutive cylinders, the canal remaining unchanged. Cellulose nitrates increase in soly. in EtOH with increase in EtOH concn., with increased modification in the nitrate due to oxidation or hydrolysis, and with decreased degree of nitration. W. H. SWANSON

The dehydration of cellulose nitrate by alcohol. KATSUMOTO ATSUKI. *J Faculty Eng Tokyo Imp. Univ.* 16, 117-33(1925).—Expts were made on the drying of cellulose nitrate by hot air, by pressing with camphor in cakes, and by replacement of  $H_2O$  by  $EtOH$ . Hot air drying decreases the stability of the nitrate and induces explosions. Drying by pressure with camphor is very effective in removing  $H_2O$  but the less stable parts of the cellulose nitrate are not removed. Drying by replacement of  $H_2O$  by  $EtOH$  is effective in the removal of  $H_2O$  and also of modified cellulose nitrate present through soln. Its removal does not increase the stability of celluloid made from the nitrate but the viscosity is increased. To prevent destruction of the colloidal nature of the celluloid the cellulose nitrate dried in this manner must not have a moisture content of over 10%. Larger amts of  $H_2O$  produce an opaque, brittle celluloid. W. H. SWANSON

The optimum working condition of celluloid from the standpoint of stability. KATSUMOTO ATSUKI. *J Faculty Eng Tokyo Imp Univ* 16, 135-56(1925); cf. *C. A.* 18, 2248.—The effect of the various steps in the manuf of celluloid on its stability was studied experimentally. Kneading of the cellulose nitrate-camphor-alc mix has no marked adverse effect on stability. Rolling affects stability adversely if the temp. is higher than  $60^\circ$ . Hot pressing reduces stability markedly above  $80^\circ$ , which seems to be a crit. temp. Increased pressure allows a decreased temp. to be used in making celluloid plastic enough for molding. Cold pressing has no effect on stability. Air drying affects stability less than hot draft drying. Proper drying consists of first air drying to prevent too rapid drying and hardening of the surface, with increased porosity of the interior, followed by a short hot draft drying to remove traces of volatile impurities. Drying always produces porosity in celluloid which appears to reduce stability somewhat. Polishing also adversely affects stability when carried on at high temp. W. H. SWANSON

Colloid chemistry of the synthesis and degradation of the cellulose framework of the plant, "lignin," and wood fiber (WISLICIENES) HD. Bituminous emulsion (Can. pat. 247,409) 22.

Preparing cellulose for esterification. J. ALTWEGG U. S. 1,543,310, June 23. Cellulose is rendered more easily esterifiable by treating it with a quantity of pure HOAc such that it forms, with the  $H_2O$  retained by the cellulose, an HOAc of 60-90% concn.

Cellulose ethers. H. DREYFUS. U. S. 1,542,541, June 16. In producing cellulose ethers, e. g., ethyl or methyl cellulose ethers, the total quantity of  $H_2O$  employed, disregarding that formed by the reaction itself, is restricted to not more than a wt. equal to that of the cellulose used. Substances are used which are capable of combining with  $H_2O$ , e. g.,  $Na_2O$ .

Films for sealing bottles, etc. G. BONWITT U. S. 1,542,434, June 16. Sealing coverings for bottles or other receptacles are formed of compound ethers, e. g., nitro-cellulose compns., which after shaping are deesterified, e. g., by  $NH_4$  sulfide.

Paper product. K. L. MOSES Can. 247,482, Mar. 10, 1925. A sheet or web of paper-like material contg. a rubber compd. is wetted and subjected to the rubbing action of presser rolls.

Paper-like product. K. L. MOSES Can. 247,431, Mar. 10, 1925. A sheet or web of high porosity and composed of relatively long loosely matted fibers is impregnated with a rubber compd.

Paper-making machine. J. D. TOMPKINS. U. S. reissue 16,100, June 23. Reissue of U. S. 1,454,606, issued May 8, 1923.

Waterproofing and grease-proofing paper. W. L. WRIGHT U. S. 1,542,539, June 16. Paper is treated with a casein and dichromate compn. and then subjected to violet or ultra-violet rays.

Waterproofed felted material. L. KIRSCHBRAUN U. S. 1,542,557, June 16. Burlap or other open mesh fabric backing is fed over a paper-making machine and united with fibrous stock and with a waterproof pitchy binder.

## 24—EXPLOSIVES AND EXPLOSIONS

CHARLES E. MUNROE

Report Chief Inspector Bureau Safe Transportation of Explosives and other Dangerous Articles for 1924. B. W. DUNN. *B. E. Rept.* No 18, 70 pp. (Mar. 1, 1925).—

Accidents in transportation on railroads in the U. S. and Canada during 1924 were due (1) 540 to acids and corrosive liquids; (2) 453 to inflammable liquids; (3) 134 to inflammable solids and oxidizing agents; (4) 75 to unlabeled semi-dangerous articles; (5) 71 to compressed gases; (6) 14 to explosives and (7) 8 to poisonous liquids and solids. The fatalities were (3) 5; (4) (5) and (6) 1 each. Injured (1) 20; (2) 20; (5) 14; (6) 3 and (4) 2. The largest property loss of \$717,969 was due to (2), followed by (3), (4), (1) and (6) in the order given, the property loss from explosives amounting to but \$5,723, although some 470,000,000 pounds entered into transportation on these railroads. The statistics are discussed at length in comparison with those given in the 9 previous annual repts., while illustrated, detailed descriptions of many of these accidents together with reports of test made in the chem. lab. are added in the appendixes.

CHARLES E. MUNROE

Second report of the Explosives in Mines Research Committee, 1924. F. L. NATHAN. Safety in Mines Research Board, *Paper No. 7*, 9 pp. (1925).—The report reviews the objects, methods and results of "empirical expts." and "fundamental research" carried out in the testing galleries at Ardeer and Eskmeals and the labs. at Sheffield. Photographic study of the ignition of gaseous mixts. has shown that the lag on the ignition of petroleum ether air mixts. by the detonation of an explosive is less than one millisecc. When a mixt. is fired, either by a high explosive or by a spark produced at a gap in the secondary circuit of an induction coil when a current in the primary circuit is ruptured, the gas mixt. is subjected locally to a high temp. and also to the influence of a wave of pressure. With a mixt. in which the speed of flame is fairly rapid there is little difference in the initial impetus given to the flame by the spark over a wide range of intensities of spark, but, with mixts. in which the speed of flame normally is slow the effect is more marked. Flames initiated by such sparks as have been described follow concentric spherical surfaces outwards from the point of ignition to the boundary of the vessel in which the explosive mixt. is contained. Though certain non-permitted explosives initiated violent coal dust-air explosions, these were not caused by permitted explosives. Great differences exist between powdered explosives and gelatinized explosives. The rate of detonation at the point of initiation increases very much more rapidly in the latter than the former. The Hopkinson pressure bar not only measures the power of an explosive, but gives some idea of the nature of the pressure wave produced. The pressure is measured by piezo elec. gages of tourmaline crystals. In the study of pressure waves resulting from detonation, it was found that a 6.8% mixt. of  $\text{CH}_4$  with air could be ignited by a rapidly applied pressure of 54 atm.; hence there exists the probability of the ignition of firedamp by a pressure wave from an explosion without the intervention of any flame. The forms and appearances of pressure waves have been examd. by a photographic method which enables the vol. of gases subjected to their action to be explored and information as to the conditions under which the surrounding atms. exists, during the short interval for which the possibility of ignition by compression obtains, secured. In studying the relative sensitiveness of various  $\text{CH}_4$ -air mixts. to ignition by a flame of known intensity impinging on them for a moment the 10% mixt. was found the most sensitive. All specimens of coal-dust tested by being blown in an air current a short distance through a Cu condenser acquired a static charge; hence whirling coal dust clouds in a mine may promote explosions from this cause.

CHARLES E. MUNROE

Coal-mining explosives. F. L. NATHAN. *Trans. Inst. Mining Eng.* 68, 453-72 (1925).—An historical review, beginning with the Commission du Griso in France constituted Mar. 20, 1877, describing the progress in developing and testing explosives for use in fiery and dusty coal mines. Especial emphasis is placed on "Investigations in connection with the gallery test" and "Scientific researches" while extensive lists of "permitted" and other explosives are given with their comps. C. E. M.

Permitted explosives: explosives authorized for use in fiery mines. W. G. Hiscock. *Ind. Chemist* 1, 172-9 (1925).—An illustrated review of the methods of testing explosives to det. their admission to the British "Permissible List," with a history of the circumstances leading to the creation of this list. The article gives statistics of production and use, together with comps. of a large number of compounded explosives. Permitted explosives are evolved from high explosives by admixing with them materials producing  $\text{H}_2\text{O}$ , or  $\text{CO}$ , or both, which serve to cool the flame. Both these are produced from  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  but, because of the offensive nature of the fumes generated by explosives contg. it in "close" workings, its use has not been widely adopted. Gelatin explosives are, because of their high density, plasticity, strength and high rate of detonation in the bore-hole, the most popular for hard ripping and in driving stone drifts, while, because of their high O balance the fumes from them are harmless. The action

of explosives of the "carbonite" type in the bore-hole approaches that of gunpowder more nearly than any other explosive known but the gases from them contain high percentages of CO and H which render them dangerous.

CHARLES E. MUNROE

Transformation of diphenylamine during the aging of smokeless powder. T. I. DAVIS AND A. A. ASHDOWN. *Ind. Eng. Chem.* 17, 674-5 (1925).—Ph<sub>2</sub>NH stabilizes smokeless powder by reaction with the HNO<sub>3</sub> and HNO<sub>2</sub> produced in its decomposition, by which the Ph<sub>2</sub>NH is converted to Ph<sub>2</sub>NNO which, by rearrangement and oxidation, yields nitro derivs. of Ph<sub>2</sub>NH. D. and A. have isolated from deteriorated U. S. pyrocellulose smokeless powder both 4-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>(2-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>)NH and (4-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>NH and also 2,4-(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>(4-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>)NH which marks the final stage of this transformation. The color reactions for this last-mentioned substance are given. With the information obtained it is possible to ascertain the present condition and past history of a smokeless powder.

C. E. M.

The explosion of firedamp. H. B. DIXON. *Trans. Inst. Mining Eng.* 68, 484-96 (1925); cf. C. A. 18, 2603.—The limits of inflammability of firedamp mixts. in long glass tubes 2 in. in diam. are for tube vertical, ignition upwards 5.4-15.1%, ignition downwards 6.0-13.4% and tube horizontal, flame at top of tube only, 5.4-14.3%. With gases flowing slowly 5% CH<sub>4</sub> was found to carry the flame. When heated throughout the limits are greatly extended; a 3% mixt. explodes when introduced into a vessel at 700° and can be fired by a sudden compression. When the O of the atm. is reduced the limits are contracted. In mixts. with N for 20.9% O the limits were 5.6-14.8, while for 13.5% O they were 6.5-6.7%. To start the flame it is necessary that a certain vol. of the mixt. be brought to a temp. at which the heat developed in the incipient chem. reaction is more than sufficient to compensate for the loss of heat to surrounding bodies; the mixt. then automatically rises in temp. at an increasing speed, since the rate of the chem. change itself increases rapidly with the temp. The ignition point is defined as the temp. at which this automatic self-heating commences. It is affected by the source of heat and the surroundings. When the solid surface acts catalytically flameless combustion of the gas may be complete before the mass reaches the ignition point. To ignite firedamp with a heated solid requires not only a sufficient temp. but a sufficient time of contact. It has even been found possible to shoot visible flame through holes in a metal plate into a firedamp-air mixt. without igniting it. The concentric tube apparatuses, firing of CH<sub>4</sub> by adiabatic compression, and the propagation of flame in firedamp are also treated of and many data from expts. on these topics given.

CHARLES E. MUNROE

Coal-dust explosions. W. MASON. *Trans. Inst. Mining Eng.* 68, 497-509 (1925).—The initiation of a coal-dust explosion is accomplished through the disto. of inflammable matter from the coal particles suspended in the air, but, for reasons yet obscure, under certain conditions dusts contg. roughly the same quantities of moisture, volatiles and ash differ markedly during the propagation of flame. The rate of development of an explosion increases as the dust cloud becomes more homogeneous until each particle reacts as a whole, the energy necessary for continued propagation being produced by the rapid formation of CO<sub>2</sub> and H<sub>2</sub>O, while the order of magnitude of the flame velocity changes from that for inflammation to that for explosive combustion. The gallery at Altofts for exptl. study of these phenomena is described with illustrations. Altofts Silkstone coal is used as the standard, it being pulverized as required to such fineness that 85% will pass a 200 X 200-mesh sieve. The quantity of dust necessary to ensure the development of an explosion cannot be calcd. accurately, since it does not burn completely during the early stages. Theoretically a cloud contg. 0.118 oz. of the "standard" dust per cu. ft. of air would be completely burned to CO<sub>2</sub> and H<sub>2</sub>O but from expt. 0.19 ounce appears the least quantity capable of developing an explosion, and this may be termed the "lower limit of inflammability" of the dust. In practice 0.4 oz. is used or, as distributed in the gallery, 1 lb. per linear foot. The theoretical quantity, 0.118 oz., thus distributed would be hardly visible. The "higher limit of inflammability" has not been ascertained, for flame has been propagated however large the excess of dust used. The development of a coal-dust explosion, the effect of admixt. with incombustible dust, and the effect of admixt. with water are discussed.

CHARLES E. MUNROE

Spontaneous combustion of coal. J. S. HALDANE. *Trans. Inst. Mining Eng.* 68, 473-83 (1925).—Although oxidation of pyrites clearly appears as a cause, yet certain kinds of coal have been found which underwent abundant oxidation with practically no oxidation of pyrites. Just what constituents of the coal thus oxidize is not yet known. After extn. with C<sub>6</sub>H<sub>5</sub>N this oxidizable material still remains in the residue. In coal fires as the coal heats up it gives off an increasing proportion of CO to the O which dis-

appears Ivon Graham's method by which 1 part of CO in 100,000 parts of air is detected underground is effective in detecting early stages of heating. A vivid, detailed description of the manner in which combustion proceeds from its inception is set forth.

CHARLES E. MUNROE

The detonation of gasoline and liquid chlorine mixtures. BENJAMIN T. BROOKS, *Ind Eng Chem* 17, 752-3(1925).—A violent accidental explosion occurring in a natural gas gasoline plant was, by surveying the paths of the projected fragments, traced to a cylinder of liquid Cl. Inquiry showed that, by error in closing valves, gasoline had been admitted to the Cl cylinder and it was suspected that the subsequent reaction had accelerated to the explosion rate. Suspicion was confirmed by the test of a standard cylinder containing 68 kg of liquid Cl, removing 22.6 kg of this Cl and replacing it with 6.34 kg of 82° Be gasoline. A recording pressure gage was attached to the cylinder from a safe distance and the cylinder warmed to 21° the more quickly to initiate the reaction. The record shows the pressure to have risen slowly at first and then with rapid acceleration until suddenly the needle swung off the chart and the mixt detonated. The cylinder was reduced to many fragments while an oak tree, 35 cm in diam and 6 m distant from the cylinder, was sheared off (Cl, C A. 19, 1631).

CHARLES E. MUNROE

A set of calibration standards for the primary experiments of ballistics. L. THOMPSON and N. RIFFOLT. *J Optical Soc Am* 10, 695-709 (1925).—The new devices cover an app for calibrating tuning forks used for the identification of small intervals of time; others for the measurement of pressure and others for the measurement of velocity. All are described with illustrations.

CHARLES E. MUNROE

The explosion of NH<sub>3</sub> with CO and O (BERSON, PARTINGTON) 6. Fire insurance and the fertilizer industry (HUBBARO) 15.

Porous material for storing explosive gases. C. HAGBERG. U. S. 1,542,573, June 23. A mixt of granulated material and powder of a fireproof substance, e. g., charcoal grains and siliceous earth, is used for storing C<sub>2</sub>H<sub>2</sub> or other explosive gases.

## 25—DYES AND TEXTILE CHEMISTRY

L. A. OLNEY

Vat dyes in America. R. NORRIS SHREVE. *Color Trade J.* 16, 127-8(1925).—A brief history of the manu of vat dyes in America.

CHAS. E. MULLIN

Chemistry and color. J. W. STURMER. *Am J. Pharm.* 97, 289-307(1925).—A popular lecture dealing with dyes, pigments and the theory of color.

W. G. O.

The magic of color. STEWART CULIN. *Color Trade J.* 16, 65-6, *Chemicals* 23, No 21, 51-2(1925).—A brief review of the early history, uses of and superstitions regarding color.

CHAS. E. MULLIN

Fast and fugitive dyes. I. J. MATOS. *Dyestuffs* 26, 17-9(1925); *Textile Am* 43, No 4, 44-5, *Textile Recorder* 43, No 506, 65, 72—General.

C. E. M.

Fast red GL from naphthol AS. A. BECHTEL. *Tiba* 3, 491-7(1925).—Fast red GL is obtained by coupling *m*-nitro-*p*-toluidine on the fiber with naphthol AS, which is the anilide of 2,3,β-hydroxynaphthoic acid. Its merits and the method of dyeing are described in detail.

A. PAPINEAU-COUTURE

Tests for blacks on cotton. C. F. GREEN. *Textile Colorist* 47, 312-4(1925).—A review of the methods of identifying cotton blacks on the fiber.

C. E. M.

Standards for testing the fastness of colors on cotton and wool. A. KERTESZ. *Chem-Ztg* 49, 109-10(1925).—A brief discussion of the various kinds of and tests for fastness. The standard tests and dye samples of the German "Fastness Commission" are discussed but not described.

WM. B. PLUMMER

The causes of dichroism in dyed fibers. A. FREY. *Naturwissenschaften* 13, 403-6(1925).—Typical colors can be produced in vegetable fibers by several elements (P, As, Sb, Bi; S, Se, Te, Ir, I; Rh, Pd, Pt; Cu, Ag, Au, Hg); the dichroism increases in each group with increasing metallic character. The lattice theory of Braun (*Ann Phys.* 16, 1, 238(1905)), which requires entire absence of dichroism for non-conductors, is, however, not generally followed. A better explanation is due to Ambrohn (Hied. *Ann* 34, 340(1888)), the optical behavior is caused by the optical properties of the

dyeing substance. Evidence is given that in the fiber the dye particles are present as adsorbed layers of directed mols rather than as microcrystals. B. J. C. VAN DER H.

"N mordant." A. BEYER *Fibz* 3, 457-67(1925).—This product, the exact nature of which is not disclosed, is a whitish, cryst mass, easily sol in hot water, but which is not perfectly homogeneous. It consists of a series of complex org acids, the most sol. of which is the most reactive. Heated above 100° it is converted into an insol. and inactive anhydride. It acts as a dibasic acid, forming insol salts with KOH and  $\text{NH}_3$ , and with all substituted ammonias, including amino and imino compds. The ppts. or lakes which it gives with dyes having an ammonia function are fast to  $\text{H}_2\text{O}$ , CaO, acid and especially to light. They are resistant to the action of  $\text{KClO}_3$ , but affected by acid reducing agents, and should not be used in Fe containers in presence of acid. It possesses strong affinity for basic and animal fibers, and little or no affinity for cotton and other cellulose fibers, its acidity being particularly troublesome in drying. In the latter case it can be used with excellent results in conjunction with certain org bases. Its method of use in various cases is described in detail. A. P. C.

Iron in the dyehouse and bleachery. W. SANDERSON *Textile Colorist* 47, 302-3 (1925).—The resistance of Fe to various reagents is discussed. CHAS. E. MULLIN.

The purification of dye-house effluents. CRISTAL LILMANN *Textilber* 6, 346-9 (1925).—After aeration, alkali treatment and rapid filtration it is suggested that fibrous material such as straw or leather scrap be used to clear the water. E. R. C.

Dyeing of vat colors. G. O. MITCHELL *Color Trade J* 16, 143-7(1925).—A discussion of vat dyes and their application to cotton. CHAS. E. MULLIN.

Dyeing of cotton piece-goods with acid coloring matters. J. MERRITT MATTHEWS *Color Trade J* 16, 61-4(1925), cf. C. 19, 1200.—The brightness, cheapness and comparative light fastness of the acid dyes occasionally make their use on cotton desirable. Only very light shades are obtainable without a special method of application. An Al mordant, either in the form of alumina or an Al soap, possibly gives the best results. Albumin and gelatin may also be fixed on the cotton fiber by means of tannic acid or steaming, but do not give as deep shades as the Al  $\text{HNO}_3$ -treated cotton also has an affinity for acid dyes. CHAS. E. MULLIN.

Dyeing of slubbing. J. S. HEUTHWAITE *Dyestuffs* 25, 169-75(1924).—General. CHAS. E. MULLIN.

Fur dyeing. C. MARTIN *Fibz* 3, 481-91(1925).—General description of the various processes. A. PAPINEAU-COUTURE.

Black dyeing of woolen goods. J. MERRITT MATTHEWS *Color Trade J* 16, 95-8(1925).—A general review. CHAS. E. MULLIN.

Process for the dyeing of mordant colors on wool. J. MERRITT MATTHEWS *Chemicals* 23, No. 21, 151-3(1925).—A discussion of the chem and colloidal theories of mordanting wool. CHAS. E. MULLIN.

Dyeing yarn for sport garments. L. J. MAYOS *Dyestuffs* 26, 33-5, *Canadian Colorist & Textile Processor* 5, 142-3, 152(1925).—A list of dyes is given. CHAS. E. MULLIN.

Printing of silk fabrics. L. J. MAYOS *Dyestuffs* 25, 158-61(1924).—Formulas and a list of dyes are given. CHAS. E. MULLIN.

Dyeing textile fibers for the hosiery trade. F. ASQUINI *Textile Am* 43, No. 4, 58-61(1925).—General. CHAS. E. MULLIN.

The dyeing of artificial silk in hosiery goods. H. B. WOLSTENHOLME *Textile Recorder* 43, No. 505, 81-3; *Chemicals* 23, No. 21, *Dyestuffs Sec.* 153-4(1925).—The dyes and dyeing methods are discussed. CHAS. E. MULLIN.

Notes on the printing of artificial silk goods. RAFFAELE SANSONE *Textile Colorist* 47, 289-93(1925).—A description of the printing processes for skeins, warps and cloth, as well as steaming. CHAS. E. MULLIN.

The anthraquinone colors on cellulose acetate. L. J. HOOLEY *Color Trade J* 16, 93-5(1925).—The Celatene dyes for acetate silk are discussed and dyeing information is given. CHAS. E. MULLIN.

The practical dyeing of celanese. G. HOLLAND ELLIS *Color Trade J* 16, 82-3 (1925).—Abstract of an address on the SRA dyes on celanese. CHAS. E. MULLIN.

Uneven dyeings on rayon. F. MÜLLER *Textilber* 6, 249-50(1925).—Irregular winding and like mech. faults account for many faults in dyeing rayon. E. R. C.

Rayon. H. JENTGEN *Kunstseide* 1, 37-8(1925).—The German term "kunstseide" rather than "kunstliche seide" serves the purpose in German of the artificial name, "rayon." E. R. CLARK.

The international rayon industry. W. A. DYER. *Kunstseide* 1, 8-10, 32-7, 55-8 (1925).—Statistical. E. R. CLARK

New spinning pump for viscose. E. GERBERICH. *Kunstseide* 1, 97-100(1925).—By operating 3 pistons, 120° out of phase, uneven pressures are avoided and more durable construction than is possible with toothed wheel pumps may be employed. E. R. CLARK

Practical notes on spinning pumps for rayon manufacture. H. JENTGEN. *Kunstseide* 1, 49-50(1925). E. R. CLARK

Rayon winding, weaving and finishing. THOMAS BROUGH AND E. SMITH. *Textile World* 67, 2719-21, 2729(1925).—A general discussion on dyeing and finishing rayon. CHAS. E. MULLIN

Spraying oil on raw cotton. H. D. MARTIN. *Textile World* 67, 2717-9(1925).—It has not formerly been the custom in cotton mills to oil the raw stock before beginning the manuf. process as is commonly done with wool, but the addn. of about 1% of processed mineral oil to the cotton in the opening room bins or preferably in the opener picker hopper, by means of an atomizer, is claimed to reduce the static and fly, give better running work, yarn of higher tensile strength and cloth with less defects, improve the condition of the card wire and keep the machinery in better order. C. E. M.

Swelling of cotton cellulose. Cotton hairs in solutions of lithium, rubidium and cesium hydroxides. GEO. E. COLLINS. *J. Textile Inst.* 16, 123-6T(1925); cf. C. A. 18, 2252.—The fact that NaOH is by far the most effective member of the alkali metal group as a mercerizing agent is confirmed. It is shown that with either Li, Na, K or Rb hydroxide the max. swelling is brought about by the soln. in which the metallic ion is fully hydrated. L. W. RIGGS

Mercerization of cotton piece-goods. M. N. CONKLIN. *Chemicals* 23, No. 21, 163-5(1925).—A general discussion of the methods, app., difficulties, etc. C. E. M.

Mercerizing linen yarns and fabrics. P. P. VICTOROFF. *Textilber.* 6, 169-72, 251-3(1925).—Tensile tests made on the basis of 100 thread strips showed that linen material is slightly strengthened by mercerizing under conditions comparable to ordinary cotton mercerizing. Warm caustic soln. is not so effective in this respect as cold, and may even weaken the fabric. The mercerization takes place practically instantaneously and when suitable tension is applied there is an increase in luster. Mercerized linen shows an increased elongation before breaking as compared with ordinary material. There is an increase in the absorptive power for dyes and tannins. Equal shades were obtained in indigo dyeing with 40% less color. E. R. CLARK

The treatment of cotton. M. N. CONKLIN. *Color Trade J.* 16, 90-1(1925).—A discussion of cotton scouring. CHAS. E. MULLIN

Finishing cotton glove fabrics. P. STRASZEWSKI. *Textilber.* 6, 250(1925).—Imitation chamois, etc., for gloves is made by mercerizing suitable boiled out fabrics without tension, the caustic being allowed to stand on the goods for 2-8 hrs. After most careful washing, the material is roughened on a special machine, dyed, and again roughened. A little glycerol in the final rinse imparts the desired handle. E. R. C.

Bleaching and finishing laces. JACOB RICHYER. *Chemicals* 23, No. 21, 165-6 (1925).—A description of the methods and app. CHAS. E. MULLIN

The action of sulfonic acids in cotton bleaching. P. P. VICTOROFF. *Textilber.* 6, 333-6(1925).—Products similar to Twitchell reagents may be used for removing fats and waxes from cotton. E. R. CLARK

The action of washing agents on cotton and linen. OTTO DISCHENDORFER. *Z. angew. Chem.* 38, 114-7(1925).—Fabrics were subjected to repeated washings with an ordinary curd soap (+ an equal amt. of  $\text{Na}_2\text{CO}_3$ ) and also with "Persil" a com. (perborate-silicate) washing compd. The strength after the 2nd, 10th, and 20th washings, in terms of the original strength, follows: linen with soap, 98.6, 94.5, 91.9, with Persil, 94.3, 75.5, 65.7; cotton with soap 96.9, 95.2, 93.3, with Persil 98.0, 91.6, 84.9. The change in the % oxycellulose, as indicated by the Cu no., varied irregularly. Either fabric after washing with Persil adsorbed methylene blue strongly from a 0.02% soln., the adsorption being proportional to the no. of washings. W. M. B. PLIMMER

Wool scouring. F. BURFORD PETRIE. *Chemicals* 23, No. 21, 167, 169, 171(1925).—A very interesting address chiefly covering the variations and improvements in the design of wool-scouring machinery. CHAS. E. MULLIN

Low-grade and damaged wool and the detection of damage in woollen fabrics. S. R. TROTMAN. *Textile Recorder* 43, No. 506, 70-1(1925).—When proteins (wool) are acted on by reagents or enzymes, hydrolysis occurs, changing the complex colloid

into a less complex and ultimately non-colloidal compds. sol. in neutral, alk. or acid solns. The incipient decompn. of wool is not visible microscopically. It possibly proceeds: proteins—proteoses—peptones—polypeptides—amino acids. Damage may be detected by the biuret or other reactions of proteoses and peptones; the elasticum reaction, C. A. 10, 1436, or Kraus and Waentig's modification, C. A. 14, 3799; or by Becke's  $\text{SnCl}_2$  reaction, C. A. 7, 1979. CHAS. E. MULLIN

(Analysis of) wool and cotton unions. C. F. GREEN. *Textile Colorist* 47, 311-2 (1925).—A discussion of the methods of detg. cotton or wool in unions. C. E. M.

Texturing silk tricot cloth. R. PRESGRAVE. *Textile World* 67, 2845-7 (1925).—A mathematical study. CHAS. E. MULLIN

Rejto method of textile testing (fibers and yarns). JOSEPH BERESI. *Textile World* 67, 2859-63 (1925).—An illustrated discussion of Rejto's methods and app. for the mech. testing of fibers and yarns, and of the graphs obtained. C. E. M.

Modern chemistry and textile fibers. HAROLD HIBBERT. *Proc. Am. Assoc. Textile Chem. Colorists* 1925, 131-9; *Am. Dyestuff Rept.* 14, 390-6.—A lecture on cellulose chemistry is followed by a discussion. L. W. RIGGS

Coöperative textile research. L. A. OLNEY. *Proc. Am. Assoc. Textile Chem. Colorists* 1925, 139-42; *Am. Dyestuff Rept.* 14, 395-8.—An address was followed by a discussion. L. W. RIGGS

Recent textile innovations. MARCEL MELLAND. *Textilber.* 6, 340-1 (1925).—Samples of cottonized flax, philana cotton and some recent Heberlein acid mercerized cotton fabrics are attached. E. R. CLARK

Recent progress in dyes and dyeing. C. E. MULLIN. *Canadian Colorist and Textile Processor* 5, 132-6 (1925).—A brief discussion of the developed bases, ionamines and dispersol dyes on acetate silk, indigosol O and OIB, soledon and other vat dyes, the neolan dyes, fast bases, rapid fast printing dyes, wool dyeing theory, moth-proofing, etc. CHAS. E. MULLIN

Stains: their origin and removal. WM. B. NANSON. *Textile Am.* 43, No. 5, 36-7, 61 (1925).—A discussion of the various stains occurring during mfg. operations. CHAS. E. MULLIN

New Cl bleaching compound (on PUYSTER) 18. Aminoalkylaminonaphthalene-sulfonic acid (U. S. pat. 1,543,569) 10. Sulfonated products of wool fat [for softening cloth] (U. S. pat. 1,543,157) 27.

Wool dye of the pyrone series. G. KÖHRES. U. S. 1,543,160, June 23. A dye is obtained from fluorescein and 2,6-xyldine, the Na salt of the sulfonic acid of which is a red powder dyeing wool fast pure yellowish red shades.

Apparatus for package dyeing. G. C. GUILD. U. S. 1,543,643, June 23. Transparent effects on cotton fabrics. R. ZIMMERMANN. U. S. 1,542,202, June 16. Soft, pliable, cotton fabrics with transparent effect are prepd. by use of a bath contg. at least 69%  $\text{H}_2\text{SO}_4$  and at least 5%  $(\text{NH}_4)_2\text{SO}_4$  (the % of acid being higher the higher the amt. of sulfate used).

## 26—PAINTS, VARNISHES AND RESINS

A. H. SABIN

The new requirements of the German National Railroad Society (Deutschen Reichsbahn-Gesellschaft) for the procurement and application of paints for steel structures. HÜLSENKAMP. *Farden-Ztg.* 30, 1440-2, 1503-5 (1925).—A general review of recently adopted specifications for paints for railroad bridges, etc. Three types of paint are recognized: those designed for protection against ordinary exposure, against exposure to chemically contaminated air, and against smoke and combustion gases. Red lead is the universally prescribed priming coat; for the remaining coats,  $\text{ZnO}$ , natural or manufactured Fe oxides, white lead or special pigments resistant to combustion products are allowed. Pure linseed oil is the required vehicle in all except the special and smoke-resistant paints. The latter paint may consist of coal or gas-oil tar if the paint is not applied to surfaces exposed to the sunlight. Acceptable deliveries of paint must conform to a previously approved sample. The specified methods of prep. the surfaces and applying the paint are discussed. (The specifications themselves are not given in detail.) F. A. WERTZ

Progress in the paint and varnish industry. IV. Paste colors. HANS WAGNER *Farben-Ztg.* 30, 1560-5(1925), cf. C. A. 19, 2276 F. A. WERTZ

Testing the hardness of a film. F. E. MOURNS. *Farben-Ztg.* 30, 1563, 1898 (1925).—An approx est of the relative hardness of a paint or varnish film may be made by examg the cut produced when the film is drawn under a cutting wheel mounted at the end of a weighted beam. Illus. F. A. WERTZ

The action of light on paint pigments. VI. Lithopone and cinnabar; a comparison. A EIBNER *Chem.-Ztg.* 49, 345-7, 370-2(1925)—A comprehensive review of the various explanations for the darkening of lithopone and red HgS in sunlight, in connection with expts with pure ZnS and HgS, indicates that the darkening is entirely due to metallic impurities interacting with the sulfide pigments. Complete references are given. F. A. WERTZ

Aluminium paint in the factory. J D EDWARDS. *Iron Age* 115, 1715(1925)—A review of the light reflecting, low thermal radiating, and heat-resisting properties of Al paints which adapt it for use in laundries and boiler rooms. F. A. WERTZ

A method of testing paint coatings for rust inhibition. HANS WOLFF *Farben-Ztg.* 30, 1317-8(1925)—The method of P Hermann (*Zentr. der Bauverwaltung* No 75-6(1923)) for detg the rust-inhibitive properties of paint coatings by measuring the elec. current passing through 2 coats of paint on a metal panel, when the panel forms one electrode and a N-KCl soln forms the other, is reviewed and criticized. This method does not measure rust-inhibitive properties, and measures relative permeability of the coatings to electrolytes only in non-pigmented films. When pigments are present, the cond. of the pigments themselves vitiates the results. Hermann's results show the test to be valueless in that he found a lithopone-rosin varnish paint more resistant than an Fe oxide-linseed oil paint, this is contrary to practical experience. F. A. W.

Printing ink and paint manufacture. OSWALD PRETZER. *Farben-Ztg.* 30, 1394-7 (1925)—A description of mixing and grinding processes. Cf. C. A. 19, 901. F. A. W.

Oil-soluble colors and their production. FR. KIRCHDORFER. *Farben-Ztg.* 30, 1625-8(1925).—Review F. A. WERTZ

Tests for hardness, glass, color and leveling of varnishes. A. H. PFUND. *Proc. Am. Soc. Testing Materials* (preprint), June, 1925, 11 pp.—Hardness is tested by a modified Brinell test in which a 2 mm steel or glass ball is forced into the varnish film. The diam. of the circle of contact between the varnish and ball is measured while the two are in contact, with a microscope supplied with a micrometer eyepiece and special illuminating device. The scale of hardness is made proportional to the load necessary to produce a circle of const. diam. Varnishes of decreasing oil length show an increasing hardness. Gloss of a varnish film is defined as the ratio of the intensity of the light reflected specularly from the surface of 45° incidence to the intensity of light reflected from a perfectly smooth surface of the same material. The reflected light is measured photometrically by means of a described app. The free surface of pure castor oil in a shallow black dish serves as the perfectly smooth, flat, standard surface. This method is particularly applicable to the study of loss of gloss due to weathering. An alternative method is based on the resolving power of the reflecting varnish surface. Two parallel wires are stretched across the beam of incident light in the app. and the angle of incidence is then varied until the wires are recognized as distinctly double. This "image angle" is recorded, and after removal of the wires, the specularly reflected light at the same angle is measured. The results by this method are little influenced by the color and brightness of the background, so that it can be successfully used on enamels. These methods cover the "normal gloss scale" from the highest glosses to flat surfaces, but are not sensitive enough to differentiate between the very highest glosses. For the latter purpose, a narrow metallic strip is placed in the path of the incident light; the ratio of the intensity of the reflected light outside the metal strip, to the light intensity of the reflected image of the strip is a measure of the gloss. For measuring color, a wedge of amber glass is placed in a reversed position beside a hollow glass wedge filled with the varnish under observation. Diffused light sent through the 2 wedges emerges through 2 slits in a slide which is moved in its groove until the colors match in a simple viewing device. The color no. is read directly from a scale graduated to correspond with the Gardner-Holdt scale, on which the instrument has been standardized. To study the leveling properties of a varnish, an arm, bearing 3 weighted needles whose points pass through the varnish film, is swept across the surface rapidly. This is repeated at 5 min. intervals on other portions of the film. Failure to level is shown by the appearance of faint undulations when the dried film is observed in reflected light. Illus. F. A. W.

Denaturants for alcohol. HERMANN VOLLMANN. *Farben-Ztg.* 30, 1319-20

(1925).—Poisoning sometimes results from the inhalation of vapors during the manu. and use of lacquers and spirit varnishes made with completely denatured alcs. The permissible denaturants in partially denatured alcs. often alter the phys. characteristics of the lacquer films produced, or for other reasons render the alc. unsuited for the lacquer industry. Isopropyl alc. and as second choice, PrOH, is proposed as a more nearly ideal denaturant for EtOH to be used in lacquers than any now permitted (in Germany). The requirements of permitted denaturants are given. F. A. WERTZ.

The quantitative estimation of resin acids. RON JUNGKUNZ *Chem.-Ztg.* 49, 391(1925).—The advantages of the Wolff and Scholz esterification method (C. A. 8, 2495) over the Twitchell method for the detn. of rosin, as reported by Davidsohn (C. A. 19, 1954) are confirmed, and comparative results on rosin oil mixts. analyzed by the former and by the McNicoll method (C. A. 15, 3216) are tabulated. The gravimetric detn. by the Wolff method gives a rosin content about 1.3% below the true value; by the McNicoll method, about 2.7% above the true value. Cf. C. A. 16, 846.

F. A. WERTZ

Hankow and Canton wood oil. HANS WOLFF *Farben-Ztg.* 30, 1383-4(1925).—The tabulated constn. on 41 authentic Hankow and 31 Canton tung oils show no significant differences between oils from these 2 sources. Higher acid nos., lower I nos., lower  $\eta$ , and slower gelatinization periods in the heat test occurred somewhat more frequently in the Canton oils, but the differences are so slight that no significance can be attached to them.

F. A. WERTZ

Chemical control of naval stores. H. C. MORRIS *Hercules Mixer* 7, 131-3 (1925).—Describes with charts, data and illustrations the practice in the plants of the Hercules Powder Co.

CHARLES E. MUNROE

Chemistry and color (STURMER) 25. Artificial turpentine (U. S. pat. 1,543,670) 22.

GARDNER, HENRY A. Physical and Chemical Examination of Paints, Varnishes, and Colors. 2nd ed. Revised and enlarged. Washington, D. C. Institute of Paint and Varnish Research. 375 pp. \$10.00 plus postage. Reviewed in *Ind. Eng. Chem.* 17, 765(1925).

Marine paint. G. W. RELYEA. U. S. 1,512,790, June 16. Red lead  $7\frac{1}{2}$  lbs., Paris green 2 lbs., and  $\text{As}_2\text{O}_3$   $\frac{1}{2}$  lb. are mixed with sufficient linseed oil, japan drier and creosote of pine to form 1 gal. of paint.

Transfer ink. H. S. SADTLER. U. S. 1,512,965, June 23. A transfer ink in powder form for producing indelible markings on fabrics comprises coumarone resin or other artificial resin which is non-saponifiable and fuses at about  $100^\circ$ , and an ink which is itself indelible.

## 27—FATS, FATTY OILS, WAXES AND SOAPS

E. SCHERUBEL

Modified Kerr-Sorber method for unsaponifiable matter in fats and grease. RAYMOND HERTWIG, G. S. JAMIESON, W. F. BAUGHMAN AND L. H. BAILEY. *J. Assoc. Official Agr. Chem.* 8, 439-42(1925).—Collaborative results indicate that modifying the Kerr-Sorber method (Jamieson, C. A. 18, 595) by washing the soap out of the  $\text{Et}_2\text{O}$  soln. with 0.2 N KOH instead of  $\text{H}_2\text{O}$  practically removes the only known objection to the method, i. e., extrn. of a small quantity of fatty acids with the unsaponifiable matter. The technique is described.

A. PAPINEAU-COUTURE

Methods for the analysis of fats and waxes. (Official for Portugal and Brazil.) *Rev. quim. pura aplicada* [3], 1, 160-3(1924).—Those methods which were different in the two countries are unified and the details for the detn. are given. M. H. SOULE.

Oxidation of unsaturated fatty acids with hydrogen peroxide and with perbenzoic acid. K. H. BAUER AND G. KUTSCHER. *Chem. Umschau* 32, 57-64(1925).—The amt. of O taken up by linolenic acid varies with exptl. conditions. With  $\text{H}_2\text{O}_2$  linolenic acid yields products closely resembling those by air oxidation. At low temp. a yellow product is formed by the absorption of 4 O atoms by 1 mol. of linolenic acid; it is sol. in petr. ether and has an I no. 91.5. By heating on the bath the yellow product changes its color to reddish brown, is then insol. in petr. ether, contains only 3 O atoms per 1 mol.

acid and has an I no. 55.9. With perbenzoic acid all double bonds disappear from linolenic acid and its I no. becomes 3.45. Analysis gives the formula  $C_{13}H_{22}O_2$  to the yellow and  $C_{13}H_{20}O_2$  to the red product but in both cases the mol. wt. in benzene soln. shows that 2 mols. have polymerized into 1 mol. The Et ester of linolenic acid does not react with  $H_2O_2$ ; with perbenzoic acid 1 mol. of the ester absorbs 3 O atoms, but its mol. wt. remains a simple mol.  $C_{23}H_{40}O_6$ , with an I no. of 28.5. Oleic acid and its Et ester are not acted on by  $H_2O_2$ ; with perbenzoic acid 1 mol. of oleic acid absorbs 2 O atoms, its mol. wt. increases and its I no. is 3.75. The Et ester of oleic acid absorbs only 1 O atom; its mol. wt. is that of a single mol.; its I no. 10.3. P. ESCHER

Acceleration of the drying of fatty oils by means of driers. A. EIBNER and FERD. PALLAUF. *Chem Umschau* 32, 81-95, 97-110(1925).—A general review with special reference to (1) artificial driers—(a) linolates and resinates, (b) linoleate-oleates, linolates, palmitates, (c) tungstates and others; (2) influence of the amt. of driers upon the drying time; (3) influence of the temp.; (4) drying energies of the individual metals; (5) Pb-Mn boiled oils, prepn. of boiled oils, polymerized oils, aging of boiled oils, theory of the drying of fatty oils and the effect of driers in the prepn. of boiled oils. P. ESCHER

Marine animal oils. H. MARCELET. *Chimie et Industrie* 13, 707-17(1925).—An outline of the prepn. and uses of these oils, with notes on difficulties and anomalies encountered in their analysis. Oils of Cetaceae gave Maumené nos. of about 27°, but with shark oil the rise was so great that the  $H_2SO_4$  was immediately decomposed, and even when dild. with olive oil they gave a Maumené of 170°. In detg. I no. via Wijs and Hübl, these oils should remain in contact with the reagent 3 and 24 hrs., resp. Oils of Cetaceae have I nos. of 11-4, and shark oils of over 300. Unsaponifiable residue should be detd. in presence of benzine, and ranges from 53 to 86%. Detn. of unsaponifiable via Halphen (treatment with  $H_2SO_4$  in presence of a volatile solvent) gave good results with cetaceous oils; but with shark oils the results varied widely according to the nature of the solvent, because of differences in the soly. of the products of the reaction. M. discovered squalene just before the war; but did not have time to investigate it or publish his results before mobilization, thereby losing priority to Tsujimoto. He found it in the oils of *Centrophorus calceus*, *C. squamosus*, *Centroscymsus coelolepis* and *Cethorinus maximus*, and also pristane ( $C_{18}H_{38}$ ) in the latter. Drying tests showed that squalene is about 5 times more active than the oil from which it is obtained. Hydrogenation tests on the various oils showed that the m. p. is raised to about 25° when the I no. has been reduced by 40-50%. A. P.-C.

Wormseed oil. J. PIERAERTS. *Mal grasses* 18, 7027-8, 7059-60, 7127-31(1925).—A review of its prepn. and compn. A sample of oil prepd. in Belgian Congo was straw-colored, had a strong camphor-like odor, a bitter, caustic taste,  $d_4^{20}$  0.9234,  $[\alpha]_D^{20} +0.42^\circ$ ,  $n_D^{20}$  1.4782, acid no. nil, sapon. no. 4.3, ester no. 4.3, I no. 96.43, incompletely sol. in 15 vols. of 70% alc., furfural reaction negative. A. PAPINEAU-COUTURE

Examination of the newer textile compounds for steeping, hucking, brightening and washing. W. HERBIG. *Z. deut. Oel-Fett-Ind.* 45, 29-30(1925).—On account of the increasing use of new fat solvents like tetralin (b. 205-7), hexalin (b. 160°), heptalin (b. 160-180°) and cyclohexanol (b. 160°) in the manuf. of Turkey red oil and textile soaps H. suggests the following modification of the usual procedure: Decompose 10 g. of the oil by boiling with dil. HCl, ext. with ether and det.  $SO_2$  in the acid soln.; absence of  $SO_2$  indicates presence of soap. Distil 50-70 g. of the oil with 150 cc. dil.  $H_2SO_4$  until the  $H_2O$  condenses in clear drops. If fatty acids have distd. over, rinse the condenser with ether into the receiver; sep. the  $H_2O$  from the distillate in a separatory funnel, evap. the ether, dry at 80° and weigh. Take up the residue with neutral alc., titrate with 0.1 N KOH and calc. as oleic acid. Ext. the fatty residue in the distn. flask with ether, evap. and weigh the residue. Dissolve this residue in gasoline alc. (1:1), titrate with 0.5 N KOH and also calc. to oleic acid and add to the first. Shake out the neutralized gasoline-alc. soln. with gasoline to ext. the unsapon. matter plus neutral fat; evap. the gasoline and weigh the residue, saponify, ext. the unsapon. matter and weigh. Any lather-promoting substances that may be present are found in the alc. soap soln. and, after the liberated fatty acids are neutralized and extd., they go into the aq. soap soln., which may then be evapd. and tested for saponin, etc. P. ESCHER

A new type of color comparator. H. S. BAILEY. *J. Oil & Fat Ind.* 2, 8-13(1925).—The Lovibond color glasses have been used by the vegetable oil chemists for some time as the basis of color grading of oils. Other standards have been tried but this seems the most practical and what is now needed for better agreement between diff. analysts is a standardization of the method of using these glasses. An instrument is described

in which the Lovibond glasses of the red and yellow scales are carried in 4 circular disks permitting the insertion of 4 glasses at a time in the optical field. Since the range of colors used in the oil industry lies almost wholly between 0 and 10 red and 0 and 40 yellow glasses covering only this range are used. Provision, however, is made for inserting darker glasses in the eye piece when needed. One disk carries the reds 0.1 to 0.9, the second 1.0 to 10.0, the third 1 to 9 yellow and the fourth a 10, 20, 30 and 35 yellow. This later because 35 yellow is the basis for all refined yellow cottonseed oils. By building up the fractional values of the glasses by superimposing 2 glasses of each color 32 cover the entire necessary range of red and yellow, taking the place of nearly 150 if only 1 red and 1 yellow were used. Although the color made by combining 2 glasses is not identical with that of the single Lovibond glass representing their combined values it is as nearly so as uniformity in different glasses of the same no. The instrument has a standard elec. light and Eastman color filter to approximate daylight readings.

H. S. B.

**The K & E Color Analyzer.** C. W. KEUFFEL. *J. Oil & Fat Ind.* 2, 14-20(1924).—The K & E Color Analyzer is a practical, direct reading spectrophotometer, intended for use in detg. the spectral transmission curves of transparent substances such as vegetable oils. These curves may be used as the basis for color specification and it is suggested they be used in grading cottonseed and other edible oils. This instrument gives measurements independent of the color vision of the observer and independent of the light with which the sample is illuminated. Diagrams upon which the detail description of the instrument is based are given and curves showing the spectral transmission of refined and bleached cottonseed oils and the usual Lovibond glasses. This app. could be used to advantage in the study of bleaching methods and the value of various fuller's earths and carbons.

H. S. B.

**A new method for the manufacture of cheap transparent soaps.** H. KASAROWSKI. *Seifensieder-Ztg.* 52, 365-6(1925).—The addn. of a soln. of K soap in hexalin to a grained soap causes a considerable transparency in the latter.

P. ESCHER

**Lathering number.** P. SCHWARZ. *Seifensieder-Ztg.* 52, 387-8(1925).—S. describes a home-made shaking app. for the detn. of the lathering no. of textile soaps.

P. ESCHER

**Lathering capacity and lathering numbers of soaps.** R. JUNGKUNZ. *Seifensieder-Ztg.* 52, 255-6, 279-80, 301-2, 323-4, 345-6(1925).—The soap solns. were prepd. by neutralizing 0.4 g. of the fatty acids from pure fats and oils by alc. alkali, evapg. the alc. and redissolving the soap in hot  $H_2O$ . Stiepel's method for detg. the lathering no. was used: the soln. was shaken for 1 min. and the lather was measured after 3 min. and 5 min. The results show that the lathering power is the smaller the greater the content of unsatd. acids; resin acids and castor oil soap yield little lather; many K soaps yield less lather than the corresponding Na soaps. While the lathering ability of soap is not a simple criterion for its cleansing power, its detn. is useful in selecting the proper raw materials for a kettle charge.

P. ESCHER

#### Gasification tests of cottonseed (MARTIN) 21.

**Sulfonated products of wool fat.** J. O. HERZOG. U. S. 1,543,157, June 23. Wool fat is dissolved in acetone,  $C_4H_8$  or other volatile solvent, the waxy and liquid fractions of the fat are sepd. from each other by cooling, and these fractions are sulfonated separately to obtain products which may be used for softening wool or treating cloth or leather.

**Treating wool scour waters.** A. J. DE RAEVE. U. S. 1,543,324, June 23. Waste waters from wool scouring are treated with lime sufficient to convert the  $Na_2CO_3$  present into  $NaOH$  and ppt.  $CaCO_3$ . The mass is heated to the b. p. while fresh, the sludge is sepd. from the liquor, and the liquor is treated at a temp. below  $35^\circ$  with  $Cl$  in equiv. proportion to the alkali present, thereby producing chloroproteins and alkali hypochlorites. The latter are neutralized with acid and the floated fats are sepd.

**Soap.** R. E. DIVINE. U. S. 1,542,438, June 16. Soap is admixed with 0.05-1.0% of diphenylamine or other similar aromatic amine, to prevent rancidity and discoloration.

## 28—SUGAR, STARCH AND GUMS

F. W. ZERBAN

**Report on sugars and sugar products, 1924.** H. S. PAINE. *J. Assoc. Official Agr. Chemists* 8, 359-63(1925).—Work by the associate referees has led to the following

recommendations, which have been approved by the assoc. (1) that in the case of products contg fructose, the method of  $H_2O$  detn by drying upon sand be carried out at  $70^\circ$  under a pressure of not over 100 mm. Hg; (2) that the official refractometric method be carried out at a standard temp of  $20^\circ$  instead of  $28^\circ$ , with the use of Schönrock's conversion table, (3) that the official ash method No. III be changed in title to "Sulfated Ash," and that results be reported as such, without application of a correction factor; (4) that the recommendations of the associate referee on polariscopic methods, regarding sucrose detn in the absence of raffinose, by acid or invertase hydrolysis, be adopted (cf following abstr.); (5) that in the method of detg sucrose by means of invertase, the directions for prep of this reagent be revised so as to conform to the latest approved practice, (6) that a method for sucrose detn. by rapid hydrolysis with invertase be added, (7) that the following new formulas for calcg. sucrose ( $S$ ) and raffinose ( $R$ ) from observed direct ( $P$ ) and invert ( $I$ ) polarization, after acid hydrolysis, be adopted:  $S = (0.514 P - I)/0.844$ , and  $R = (0.33 P + I)/1.563$ , (8) that in the detn. of sucrose by the double diln method the true direct and invert polarizations be calcd. by deducting the polarization of the undiln soln. from 4 times the polarization of the diln soln., (9) that in the detn. of com glucose results be reported in terms of glucose solids, the factors 211 and 196 being used, instead of the present 175 and 163, resp.; (10) that the subdivision on maltose products be amplified so as to include all starch conversion products, (11) that work be continued as suggested by associate referees. The revised texts of methods are given in full.

F. W. ZERBAN

Report on polariscopic methods, 1924. F. W. ZERBAN. *J. Assoc. Official Agr. Chemists* 8, 384-402(1925)—Exptl work has shown that the change in the Clerget divisor with concn must be based on total sugar concn and not on that of sucrose alone. Jackson and Gillis' methods No. II and IV (C. A. 14, 2561) give the same results as the invertase method in the analysis of mixts. of sucrose and invert sugar, but yield too high results when reversion products are present. The following formulas, for sucrose detn in the absence of raffinose, are proposed as a result of the investigation: (1) for Schreiffeld's modification (C. A. 15, 186) of the acid hydrolysis method at room temp, sucrose =  $100(P - I)/(143 + 0.0676(m - 13) - 0.5T)$ , where  $P$  is the direct,  $I$  the invert polarization,  $m$  the g. total sugars (or total solids) in 100 cc of the soln. read, and  $T$  the temp., (2) for Schreiffeld's modification at  $67-69.5^\circ$ , the same formula, but with Clerget const. 143.2, (3) for invertase inversion, the same formula, but with Clerget const. 142.0. Direct and invert polarization must be made at the same diln. Other minor changes in the methods are proposed, and the full text of the modified methods is given in the recommendations for adoption.

F. W. ZERBAN

Sugar production in the 1924 campaign (Java). J. VAN HARREVELD. *Arch. Suikerind.* 33; *Mededeel. Proefstat. Java-Suikerind.* No. 3, 105-23(1925)—Statistical tables show quantity of cane ground, and various grades of sugar and of molasses produced by each factory, also comparison of totals and averages with former yrs since 1910.

F. W. ZERBAN

Statistics of the 1924-25 campaign (Mauritius). M. KOENIG. *Rev. agr. Maurice* 2, 488-9(1925), cf C. A. 19, 413—Tables show total sugar production each yr. since 1920 by districts, also sugar produced % cane, and white sugar % total sugar, since 1918.

F. W. ZERBAN

Report on chemical methods for reducing sugar, 1924. R. F. JACKSON. *J. Assoc. Official Agr. Chemists* 8, 402-4(1925).—It is recommended to make a study of some of the promising methods proposed recently; to det. the limits of accuracy of present methods, to verify the standard conversion tables, and to reduce the large no. of methods now endorsed by the assoc.

F. W. ZERBAN

Final report of the mill and fuel control for 1924 (Java). ANON. *Arch. Suikerind.* 33; *Mededeel. Proefstat. Java-Suikerind.* No. 2, 27-103(1925), cf. C. A. 19, 414—The same data are given as in the previous report. The av. sugar yield was 0.1-0.7 better than in 1923, varying with the equipment. Again imbibition used was higher than in 1923, and juice lost in bagasse correspondingly lower. The total consumption of calories was less. The amt. of wood used has been further reduced, while that of the by-products of plantation and factory has been extended.

F. W. ZERBAN

Computation by graphic methods. B. A. RÖHRICH. *Arch. Suikerind.* 33, 393-5(1925)—It is shown how the different mill control data can be arrived at by plotting instead of calcn (diagram).

F. W. ZERBAN

Thomas and Petree process. L. BAESSAC. *Rev. agr. Maurice* 2, 409-9(1925)—A brief description of the process is given, and the conclusions of Greenfield (C. A. 19, 747) are reviewed. It is doubtful whether the process gives as satisfactory results in white sugar manuf. as in that of raw.

F. W. ZERBAN

Choice of boiler pressure and of type of turbine in the electrification of sugar factories, considering also a change to pressure evaporation. W. HEUCKE *Siemens-Z.* 5, 158-61(1925). F. W. Z.

Report on drying, densimetric and refractometric methods (for determining moisture in sugar-house products). J. F. BREWSTER *J. Assoc. Official Agr. Chem.* 8, 375-84(1925).—Collaborative work indicated that none of the methods generally used for the detn. of solids by drying is to be regarded as uniformly reliable, sirups and molasses being particularly difficult to analyze in this respect. A. P. C.

Root disease of sugar cane. E. F. S. SHEPHERD *Rev. agr. Maurice* 2, 418-20 (1925).—A general article, with bibliography. F. W. ZERBAN

Cane-juice-settling tank. C. W. RICKSTUHL. U. S. 1,543,621, June 23  
Apparatus for continuous clarification of sugar cane juice or other liquids. F. J. CASABLANCA and M. F. GALDO. U. S. 1,512,666, June 16.

## 29—LEATHER AND GLUE

ALLEN ROGERS

Imperfections in leather caused by microorganisms. J. A. WILSON and GUIDO DAUB. *Ind. Eng. Chem.* 17, 700-2(1925).—Hog grain is the result of bacterial decomposition of the fibers connecting the thermostat and reticular layers of the raw skin, which may occur without any other damage being apparent. Veins are caused by bacterial action in the channels occupied by the blood vessels. Freckle-like spots and buffed effects are produced by bacterial action on the fibers of the grain surface of the raw skin. After tanning, the greatest damage is done by molds, which grow readily on damp leather, causing spots and discoloration. J. A. WILSON

Preparation of artificial bating agent. M. KAWABATA. *Report Osaka Ind. Research Lab. (Japan)* 3, No. 9, 1-17(1921).—On the theory of Wilson (*C. A.* 15, 191) that the essential function of the bating process is to remove elastin from the hide, K. prepd. pancreatin from the steer and added various amts. of  $\text{NH}_4\text{Cl}$  and phosphate, which K. found to be contained in American products, and studied their effects on tryptic power of the pancreatin on casein, and on the histological structure of hide. The results show that a mixt. of 50 parts pancreatin, 10 parts  $\text{NH}_4\text{Cl}$  and 0.1 part  $\text{NaH}_2\text{PO}_4$  makes as good bating agent as those sold on the market. However, this artificial bating agent is much more expensive than natural bating agents, such as excreta. S. T.

Salt stains as an autolysis phenomenon. H. PERICAUD. *Cuir tech.* 14, 208 (1925).—If blood is allowed to coagulate in the skin, neither salt nor specific antiseptics can prevent the formation of salt stains. The stains result from autolytic changes in the coagulated blood. H. B. MERRILL

Applied science in gelatin manufacture. CHARLTON TYLER. *Chem. Met. Eng.* 32, 553-6(1925). E. H.

Reactions in solutions of quinone. L. MEUNIER and M. QUEROIX. *J. Soc. Leather Trades' Chem.* 9, 26-31(1925).—See *C. A.* 19, 747. E. J. C.

Determining H-ion concentration (HUGONIS) 2. Sulfonated products of wool fat [for treating leather] (U. S. pat. 1,513,157) 27.

Tanning. D. D. JACKSON, A. ROGERS and T. HOU. U. S. 1,541,819, June 16.  $\text{FeSO}_4$  or other ferrous salt is oxidized to the ferric state, *e. g.*, by  $\text{Cl}_2$  and  $\text{Na}_2\text{CO}_3$  or other alkali is added to produce a basicity between the ratios of 5 to 6 and 3 to 4 equivs of the mineral acid radical to the ferric ion in the oxidized solu. used for tanning.

## 30—RUBBER AND ALLIED SUBSTANCES

C. C. DAVIS

The resilient energy criterion as applied to the shape of the rubber stress-strain curve. WM. B. WIGGAND. *Ind. Eng. Chem.* 17, 623-5(1925).—The stress-strain curve of soft rubber mixts. is usually concave to the stress axis, which means that the resilient energy in terms of the area under the stress strain curve (*cf.* *C. A.* 14, 2732) is less than that of a material which follows Hooke's law to the yield point. Furthermore expts. indicate that this area is the best single criterion of the resistance to abrasion.

Therefore the more nearly the stress-strain curve approaches a straight line the more resistant the rubber is to abrasion. Accordingly it is proposed to utilize the ratio of the area lying between the stress-strain curve and the elongation axis to the corresponding area when the stress-strain curve is a straight line as a criterion of the resistance of a rubber mixt. to abrasion. This so-called concavity factor is dependent to but a slight degree upon the type of rubber or upon the cure but it is profoundly influenced by the amt. of filler. The larger the amt. and the finer the particles of the filler the greater is its power to increase the concavity factor. With all fillers the concn. of filler at which the concavity factor reaches 100% exceeds the concn. at which the optimum reinforcing action, based on the max. resilient energy, is attained. Graphs show the influence on the concavity factor and on the resilient energy of increasing amts. of C black, ZnO,  $\text{MgCO}_3$ , china clay, whiting and barytes. Rubber contg. C black had the highest resilient energy of any filler at a concavity factor of 100%. The ideal and max. reinforcing action presupposes a filler with which the max. resilient energy and a concavity factor of 100% are reached at the same concn. C. C. DAVIS

The influence of inorganic and organic accelerators of vulcanization on the temperature of rubber mixtures during vulcanization. III. F. KIRCHHOFF. *Gummi-Ztg* 39, 892-5(1925); *J. Soc. Chem. Ind.* 44, 367B; cf. C. A. 19, 1965.—If the  $\text{Me}_2\text{CO}$ -sol components of *Hevea* rubber are heated with aq. alkalis to remove volatile bases, are then extd. with light petroleum to remove the unsaponifiable resins, and the resin acids are liberated by addn. of  $\text{H}_2\text{SO}_4$ , the reintroduction of these resin acids into the extd. rubber gives a product which combines with S at about 0.5 the rate shown by a similar mixt. of extd. rubber with the whole of the  $\text{Me}_2\text{CO}$ -sol. substances. In the presence of PbO the increase in the rate of vulcanization of rubber with rise in temp. shows a marked change in the neighborhood of 167°, for above this temp. the rubber resins begin to react with S and form  $\text{H}_2\text{S}$ , which then reacts exothermically with the PbO. The effect of org. accelerators such as urea, *p*-toluidine, piperidine, anilina, thiocarbonylurea and piperidine-piperidine-1-carbothionolate on the internal heating during vulcanization is greater than that of similar proportions of inorg. accelerators. The attainment of a high degree of vulcanization is also accompanied by a high internal development of heat. The additional presence of MgO favors the vulcanization process, but appears to have a depressing action on the internal heating, except with urea. Both the thermal and the accelerating effects apparently depend upon the basic character of the substances added or of their decompn. products. When heated with S at 160-70° naphthylamine gives a yellow product of the compn.  $(\text{C}_{10}\text{H}_7\text{NH})_2\text{S}_2$ , and hexamethylenetetramine gives cyanogen trisulfide  $(\text{CN})_2\text{S}_2$  and its derivs. These compds have little if any vulcanizing action, but their formation during vulcanization is accompanied by the formation of active S in the form of  $\text{S}_x$ . Acceleration of vulcanization by org. bases and similar compds is considered to depend upon the formation of active  $\text{S}_x$  from ordinary S by chem. and thermal action (cf. C. A. 15, 1421).

C. C. DAVIS

Is raw rubber partially crystallized? J. R. KATZ AND K. BING. *Z. angew. Chem.* 38, 439-41(1925).—Based on Röntgen spectrographs it has already been shown (cf. C. A. 19, 2144) that raw rubber is amorphous until stretched, whereupon it partially crystallizes. It is possible that the absence of crystals in some of the previous samples was due to earlier heating, plasticizing or other mech. treatment, so further types of rubber were examd. for the presence of crystals. In first latex crepe, thick pale sole crepe, light brown crepe, ribbed smoked sheets and above all in specially prepd. light and brown rubber (Patentgummi) distinct evidences of crystals were found, whereas their presence was doubtful in para rubber and none was observed in dried latex. Mastication of rubber contg. crystals, either to a limited extent or until all plasticity was gone, caused the disappearance of the crystals. On subsequent stretching they reappeared. With the rubber plasticized very soft, the elasticity was recovered by cold vulcanization before examn. for crystals. Heating at 100° for 20 min. with no mech. treatment also caused the disappearance of the crystals. On cooling this latter sample and another which contained no crystals to -10° for 2 days or even to 0-2° for 4 days and then warming to room temp., crystals did not reappear. Further expts. indicated that the crystals which appear in regular alignment on stretching form independently of those which may already be present and that the latter retain their original orientation during the stretching. C. C. DAVIS

The Joule effect. R. W. LUNN. *J. Soc. Chem. Ind.* 44, 247-53T(1925).—A discussion of the Joule effect in rubber and its relation to the coeff. of expansion, to the elastic modulus and to the hypothetical structure. It is suggested by Schmulewitsch (*Ann. Physik* [2], 144, 280(1872)) that the retraction of rubber under tension with rise

in temp. is due to an increase in the elastic modulus, in which case the stress-strain curve should move with rise in temp toward the stress axis. Expts. however indicate that the stress-strain curve actually moves in the opposite direction, the magnitude of the change being shown in 1 case where a difference in elongation at 300% extension of less than 0.5 cm. in 7 cm. was found between 20° and 30°. It is assumed that the decay in tension in all rubber which is elongated increases with rise in temp. and that the Joule effect is masked by the flow under load. Though only speculative, the spheroidal theory already suggested (cf. Lunn, *C. A.* 17, 1903), extended to include a viscous liquid in which the particles are suspended, is useful in explaining the Joule effect (cf. Chauveau, *Compt. rend.* 1899). Extension increases the intermol. spaces of the continuous liquid medium, with consequent cooling like a gas. If the liquid wetted the particles but slightly, cooling would be continuous as the elongation increased. But in rubber the affinity between the particles and the liquid is assumed to be great enough so that after a short extension the particles are distorted and compressed, with the generation of heat. Both effects increase independently with increase in extension and either can be made to predominate by the proper rate of heating the rubber. Also in *India Rubber J.* 69, 851-4 (1925) with portrait of Joule.

C. C. DAVIS

Modern materials used in rubber compounding. A. A. SOMERVILLE *Rubber Age* (London) 6, 85-93 (1925).—A discussion of some of the newer compounding materials, including clay and ultra-rapid accelerators. The paper is followed by an open discussion.

C. R. PARK

Breaking down plantation rubber with naphtha. ANON. *Rubber Age* (London) 6, 79-80 (1925).—Naphtha is added during milling to shorten time of breaking the rubber. The effect is not permanent and the phys. properties of the rubber so treated are equal to the control.

C. R. P.

The manufacture and testing for accelerator action of the di- and tri-arylguanidines. I. W. J. S. NAUNTON, *J. Soc. Chem. Ind.* 44, 243-7T (1925).—A review and discussion of methods, some patented, for prepg. arylguanidines, with particular reference to di- and triphenylguanidine. The diarylguanidines, because of the volatility of the  $\text{NH}_2$ , used in the condensation, can best be prepd. by a modification of the  $\text{NH}_4$  salt method of Forster (*Ann.* 175, 32). The triarylguanidines can best be prepd. by the usual lab. method in which the  $\text{EtOH}$  is replaced by a cheaper solvent, or merely by an excess of the aryl amine. To det. the activity of an accelerator without resort to rubber lab. equipment, either of 2 procedures can be used when the accelerator is sol. in  $\text{C}_6\text{H}_6$ , depending on whether it is neutral or basic. An approx. index of the activity of a  $\text{C}_6\text{H}_5$ -sol. accelerator can be obtained from its effect on the viscosity of a  $\text{C}_6\text{H}_5$  soln. of rubber (cf. LeBlanc and Kröger, *C. A.* 16, 175). Nearly fill glass tubes 30 cm. long and 2 cm. in diam. with a 2%  $\text{C}_6\text{H}_5$  soln. of rubber, mix in the accelerators in definite amts. and det. the relative times for the air bubbles to rise on inverting the tubes. The method is reliable only with compds. of similar chem. compn. (cf. Eggink, *C. A.* 18, 181). The relative activities can also be detd. by comparing their accelerating action on the formation of a gel in a  $\text{C}_6\text{H}_5$  soln. of rubber and  $\text{SnCl}_4$ . This test is applicable only to neutral compds. like thioureas and at the same time only to those of similar chem. compn. The method of Whitby and Cambron (*C. A.* 17, 3808), though useful for ultra-accelerators, was unreliable with less active ones, and that of LeBlanc and Kröger (*loc. cit.*) using  $\text{S}$  and  $\text{C}_6\text{H}_5\text{Cl}$  was also useless. The accelerating activity of the diarylguanidines increases with increase in the mol. wt. of the substituent aryl groups. With ditolylguanidines, the *p*-compd. is more active than the *o*-compd. and with the dixylylguanidines the *m*-compd. is slightly more active than the *o*-compd. These dixylylguanidines are both more active than either of the ditolylguanidines. Di-*p*-tolylguanidine is more active than di-*o*-tolylguanidine (cf. Scott, *C. A.* 17, 1430) and diphenylguanidine is more active than the triarylguanidines. Tetramethyldiaminodiphenylguanidine is much more active than diphenylguanidine and is equally free from a tendency to preclude rubber at low temps.

C. C. DAVIS

Rubber articles from latex. E. HOPKINSON and W. A. GIBBONS. U. S. 1,542,388, June 16. In making surgeon's gloves, tire tubes, overshoes or other rubber articles, the surface of a form is brought into contact with latex, moisture is removed from the portion of latex in contact with the form and the material is dried and vulcanized. The form used may be made of unglazed porcelain.

Drying latex. E. HOPKINSON. U. S. 1,542,939, June 23. Films of latex or similar materials are formed and broken up into particles, e. g., by spreading on a wire screen and blasting with air, and the dispersed particles are dried by air or  $\text{CO}_2$ .

Grinding hard rubber. W. C. HOOVER and A. DWYER. U. S. 1,542,346, June 16. Hard rubber is crushed in an inert fluid such as washed combustion gases at an elevated temp. (which may be about 105-150°) to facilitate the grinding, and the ground particles are then sepd. from the inert fluid.

Vulcanization of rubber. A. C. BURRAGE, JR. Can. 247,103, Feb. 24, 1925. Rubber is heated with a vulcanizing agent and a mixt. of methylene *p*-toluidine and tri-*o*-tolylguanidine. Cf. C. A. 19, 1507.

Vulcanizing rubber. C. O. NORTH. Can. 247,485, Mar. 10, 1925. Rubber is vulcanized with a vulcanizing agent and the aldehyde deriv. of a compd. formed by the action of an excess of aldehyde on an amine.

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# CHEMICAL ABSTRACTS

Vol. 19.

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No. 16

## 1—APPARATUS AND PLANT EQUIPMENT

W. L. HADGER

Acetylene generator. M. BERGER. *Apparatebau* 37, 145-6(1925); 2 cuts.

J. H. MOORE

Technical notes on evaporators. HARTLAND SEYMOUR. *Ind. Chemist* 1, 254-8 (1925).

A new really improved laboratory manometer. L. EBERT. *Z. angew. Chem.* 38, 493(1925).—This article describes a lab. manometer which may easily be cleaned and refilled if gas or liquid becomes entrapped.

D. E. S.

A modified form of the Soxhlet extraction apparatus. B. KÖHLER. *Collegium* 1925, 187-8.—The receiving vessel (A) and the vessel contg. the sample to be extd. (S) are at the same level and are connected by 2 horizontal tubes. The app. is pivoted at the middle of the larger tube so that at the end of the extn. A can be raised with respect to S and the solvent distd. into S and thus be recovered. S can be immersed in a bath at any desired temp.

I. D. CLARKE

An improved electrically heated melting-point apparatus. F. A. MASON. *Chem. & Industry* 44, 577(1925).—This consists of a wire-wound cylinder provided with a hole for the thermometer, another for the m. p. tube and a third hole for observing the substance under test. The instrument is useful as high as 400°.

D. E. SHARP

Ebullioscopic apparatus. W. SWIENTOSLAWSKI AND W. ROMER. *Bull. Intern. Acad. Pol. Sci. Letters* 1924, 59-62.—The modified app. previously described (*C. A.* 18, 2444) is altered by the introduction of a short glass-tube sleeve to surround the thermometer bulb. This improved app. admits of the detn. of the b. p. with an accuracy of  $\pm 0.0015^\circ$ . In making ebullioscopic measurements, 2 such instruments should be used, so that the b. p. of the solvent and soln. may be detd. simultaneously.

B. C. A.

Devices for preventing delay in boiling. JULIUS ÖBERMILLER. *Z. angew. Chem.* 38, 491-3(1925).—This article is a discussion of claims to novelty and the advantages of his "boiling rod." Cf. *C. A.* 18, 2979.

D. E. S.

An interfacial tensiometer for universal use. P. LECOMTE DU NOUY. *J. Gen. Physiol.* 7, 625-31(1925).—A modification of the tensiometer (cf. *C. A.* 13, 1549) for the measurement of the interfacial tension between liquids.

C. H. R.

Apparatus for the rapid measurement of the surface tension at a liquid-liquid interface. Influence of temperature. P. LECOMTE DU NOUY. *Compt. rend.* 180, 1579-80(1925); cf. preceding abstract.—The surface tension at a  $\text{CS}_2\text{-(Et)}_2\text{O}$  interface, as well as that at an octyl alc.-heptaldehyde interface, increases with temp.

R. L. DODGE

Improvement in thickening and water clarification. NOEL CUNNINGHAM. *Trans. Am. Inst. Chem. Eng.* June, 1925 (advance copy) 3-9.—The superthickener consists essentially of a cylindrical-walled tank having a permanent porous false bottom upon which is supported a destructible filter bottom several feet thick and composed of fine granular particles. As the solid content of the feed increases the superthickener functions successively as a clarifier, a thickener-filter and filter. The operation in each case is outlined. The action in the superthickener is to eliminate segregation during treatment and under-flow from it is too thick to allow segregation in transfer, storage or further treatment. The superthickener handles some old problems to better advantage, makes possible soln. of some unsolved, and is particularly applicable to dil. suspensions of difficultly settling or gummy colloids.

W. H. BOYNTON

A laboratory ozonizer yielding high concentrations of ozone. I. I. SMITH. *J. Am. Chem. Soc.* 47, 1844-50(1925).—A lab. ozonizer is described capable of giving ozonized O contg. about 15% of ozone at a rate of over 4 g. of ozone per hr. O is ozonized by a silent elec. discharge across an annular space 3 mm. wide and 48 cm. long, through which dry O is flowing. The discharge is effected with a 0.055-kva. transformer operat-

ing on a 110-v 60-cycle primary current. The voltage in the secondary is about 8000. The inside glass wall of the annular gas space is provided with a Hg electrode. A water bath surrounding the outside glass wall serves as the second electrode and as a cooling medium. The gas flows through 3 such tubes in series (Berthelot tubes). R. L. D.

A critical study of the Burrell indicator for combustible gases in air. L. H. MULLIGAN. *Bur. of Mines, Tech. Paper* 357, 1-40 (1925).—This paper describes in detail the Burrell indicator, gives directions for operating, and results obtained in tests in mine air. Its satisfactory use requires that the gas to be tested be practically insol. in  $H_2O$ . The instrument is most accurate in detg.  $H_2$ , gives good results on  $CH_4$ , and is useful on petroleum vapors. A new switch design is described which reduces chance of burning out the glow because of over-voltage of freshly charged batteries. The paper covers in detail possible sources of error in testing, and use of the indicator for  $H_2$  and gasoline vapor. Exptl. calibration of the indicator verifies the soundness of the theoretical calibration. D. E. SHARP

The measurement of viscosity, especially of lubricating oils. RICHARD VON DALLWITZ-WEGNER. *Z. tech. Physik* 6, 221-5 (1925).—Several of the common types of viscometers are described. A viscoscope is described by means of which the dependence of the viscosity upon the pressure may be detd. J. H. PERRY

Plants for drying. W. GRAULICH. *Chem.-Ztg.* 48, 876-7 (1924).—A presentation of the elementary principles involved in designing and constructing plants for drying various substances. W. C. ESHAUGH

The design, construction and use of a constant-humidity room. R. G. PARKER AND D. N. JACKMAN. *J. Soc. Chem. Ind.* 44, 223-33T (1925).—The necessity for and requirements of a small const.-humidity room for exptl. work on textiles are dealt with at some length. The room designed by P. and J. is 6'  $\times$  7' and 7' high, and was built against 2 inner walls of a lab. The construction, control and operation of the hair hygrometer used, the method of temp. control, the circulation of air together with the methods of humidifying and drying same, and the behavior of the whole installation under different working conditions are all gone into in considerable detail. The article contains numerous photographs and drawings. E. G. R. ARDAGH

### Microbalance (HARTUNG) 3.

Apparatus for purifying liquids. K. J. SVENSSON and K. A. P. NORLING. *Swed.* 58,730, May 13, 1925.

Centrifuge with two perforated mantels. SVENSKA SOCKERFABRIKS AKTIEBOLAGET. *Swed.* 58,276, Feb. 18, 1925. The inner mantel is, provided with a gas inlet. It can be lifted up from the centrifuge, producing an opening for the discharging funnel in the bottom of the app. The materials are charged between the two mantels.

Drying coarse materials. SVENSKA SOCKERFABRIKS AKTIEBOLAGET. *Swed.* 58,275, Feb. 18, 1925. A system of transporting belts.

## 2—GENERAL AND PHYSICAL CHEMISTRY

GEORGE L. CLARK AND BRIAN MEAD

Bibliography of bibliographies on chemistry and chemical technology 1900-1924. C. J. WEST AND D. D. BEROLZHEIMER. *Bull. Nat. Research Council* 9, Pt. 3, No. 50, 308 pp (1925). E. H.

Chemical historical notes. A hundred years of benzene. ERNST COREN. *Chem. Weekblad* 22, 319-25 (1925).—Biographical notes on Faraday are included. E. H.

Chemical education and investigation in China. P. C. MABEE. *China J. Science & Arts* 3, 297-302 (1925). W. H. ADOLPH

Frédéric Chaplet (1860-1925). LÉON GUILLET. *Rev. métal.* 22, 310 (1925).—An obituary with portrait. A. PAFINEAU-COUTURE

Norway as a chemist. W. J. POPE. *Chemistry & Industry* 44, 630-3, 633-5 (1925). E. H.

Atomic weight of chlorine. (MILLER) E. GLEDITSCH. *J. chim. phys.* 21, 456-60 (1924).—No difference could be detected in the at. wts. of Cl contained in carefully purified  $AgCl$  prepd. from (a) volcanic  $NH_4Cl$  produced in an eruption of Vesuvius, (b) water from a depth of 1573 m. in the Calumet and Hecla mines near Lake Superior, and (c) ordinary  $BaCl_2$ . B. C. A.

The atomic weight of silicon and the analysis of silicon tetrachloride. O. HÖNIG-SCHMID AND M. STEINHEIL. *Z. anorg. allgem. Chem.* 141, 101-8(1924).—The mean value of the at. wt. of Si is  $28.105 \pm 0.003$ . This value agrees with the wt. of 28.111 detd. by Baxter (cf. *C. A.* 14, 2109). The detn. is based upon the proportion  $\text{SiCl}_4$ , 4Ag. L. M. HENDERSON

Determination of the atomic weight of bismuth. A. CLASSEN AND GEO. STRAUCH. *Z. anorg. allgem. Chem.* 141, 82-91(1924).—The av. value of the at. wt. of Bi is 208.989. Bi triphenyl was mixed with oxalic acid and carefully heated to drive off the benzene. The temp. was very gradually increased until  $350-400^\circ$  was obtained, when O was admitted to the system, and the temp. raised to  $750^\circ$ . The Bi was weighed as oxide. L. M. HENDERSON

Copper oxide and the atomic weight of copper. RUDOLF RUER AND KURT BODE. *Ber.* 58B, 852-9(1925), cf. *C. A.* 18, 3128.— $\text{CuO}$  is proved to be non-dissociated and free from occluded gas, after having been heated to  $1000^\circ$  8 times in air and slowly cooled, and then heated at  $700^\circ$  in O to const. wt. It is then reduced in  $\text{H}_2$  and the Cu heated to const. wt. at  $750^\circ$ . The Cu contains no  $\text{H}_2$ . The at. wt., so detd., is 63.546. R. J. HAVIGHURST

Precise determination of the atomic mass of lithium 6 (method of Aston). J.-L. COSTA. *Compt. rend.* 180, 1661-2(1925).—By careful comparison with the mass of He (= 4.000), 2 plates gave for  $\text{Li}^6$   $6.009 \pm 0.002$  and  $6.010 \pm 0.002$ . G. L. CLARK

The characteristics, especially density, cubical contraction and quality, of refined aluminium from Grevenbroich. R. HOFFMAN AND W. STAHL. *Metall u. Erz.* 22, 103-7(1925).—Three values for  $d_{13}^{15}$  were 2.7085, 2.7026 and 2.7074 (av. 2.7062);  $d_4^{760}$  was 2.4459. The cu. coeff. of contraction between  $0^\circ$  and  $760^\circ$  was 0.0001422 and 0.0001412 (two detns.). Hardness by the Brinell test was 24.2 kg./mm.<sup>2</sup>. The "hard plate" metal gave for  $d_4^{16}$  2.7165, hardness 17.4, for a plate heated and cooled quickly  $d_4^{18}$  = 2.7152, hardness 9.5; for a plate heated and cooled slowly  $d_4^{18}$  = 2.7108, hardness 9.3. C. G. KING

Germanium. XI. Germanium glasses. Preliminary note. L. M. DENNIS AND A. W. LAUDENGAYER. *J. Am. Chem. Soc.* 47, 1945-7(1925).—Four different glasses were prepd. with the same mol. compn. as ordinary glasses except  $\text{GeO}_2$  instead of  $\text{SiO}_2$ . They had higher  $n_s$  and lower  $m_p$ , but were otherwise similar. Fused  $\text{GeO}_2$  resembled fused quartz. Cf. *C. A.* 19, 1832. A. W. FRANCIS

The electric moments of the molecules of monocarboxylic acids and their esters. C. P. SLYTH. *J. Am. Chem. Soc.* 47, 1894-900(1925); cf. *C. A.* 17, 2382.—Elec. moments of the acids and esters have been calcd. from their structures under appropriate assumptions, and found in good agreement with values calcd. from mol. refraction. Deviations were ascribed to the mutual effect of bulky groups in the mol. A. W. F.

Atoms and isomorphism. A. N. WINCHELL. *Science* 61, 553-7(1925).—Utilizing the Bragg values for "at. domains" W. shows that the size of atoms is more important in detg. isomorphism in crystals than is valence. Thus  $\text{NaAlSi}_3\text{Si}_2\text{O}_{10}$  and  $\text{CaAl}_2\text{Si}_2\text{O}_7$  are isomorphic, though valences are different, because sizes are comparable. Numerous other examples, largely minerals, are cited. G. L. CLARK

Transformation temperature of thallium. G. ASAHARA. *Sci. Papers Inst. Phys. Chem. Research* (Tokyo) 2, 253-71(1925).—The transition temp. of pure electrolytic Tl was measured by the method of thermal analysis. The mean of 24 observations is  $232.69^\circ$  for heating and  $232.39^\circ$  for cooling with the general av. of  $232.5 \pm 0.5^\circ$ . A second small max. pt. observed in the inverse-rate heating curves is traced to the particular distribution of temp. in the metal specimen due to the propagation of the transformation. JAMES M. BELL

Effect of allotropic change on grain growth in thallium. GENSICHI ASAHARA. *Sci. Papers Inst. Phys. Chem. Research* (Tokyo) 2, 273-6(1925).—X-ray Laue photographs have shown (*C. A.* 14, 2326) that at the transition temp. of Tl there is an abrupt change of pattern. The present paper shows from such photographs that a crystal of Tl when once developed does not disintegrate into smaller ones when undergoing the allotropic change, that is, the lattice structure glides with ease from one type to another without fracture. JAMES M. BELL

A study of crystal structure and its applications. V. W. P. DAVEY. *Gen. Elec. Rev.* 28, 342-8(1925); cf. *C. A.* 19, 2149.—In this instalment the Bragg method of crystal analysis is presented. C. G. F.

X-ray analysis of the solid solutions of potassium chloride and potassium bromide. T. SASAHARA. *Sci. Papers Inst. Phys. Chem. Res.* (Tokyo) 2, 277-86(1925).—The

results, proving the law of additivity (mol. % vs. d. of solid soln. linear), check those of Havighurst, Mack and Blake (*C. A.* 19, 755).

G. L. CLARK

X-ray analysis of electrolytic brass. HATIME NAKAMURA. *Sci. Papers Inst. Phys. Chem. Res. (Tokyo)* 2, 287-32(1925).—The lattice const. of an electrolytic brass contg 82.48% Cu, viz.  $3.62 \times 10^{-8}$  cm., is identical with that for cast brass contg. 82.85% Cu. Hence the solid soln. of Cu and Zn is formed by an electrolytic process as easily as by fusion or other processes.

G. L. CLARK

X-ray examination of inner structure of strained metals. III. Copper and aluminium under extension, compression and torsion. AKIMASA ONO. *Mem. Coll. Eng. Kyushu Imp. Univ.* 3, 195-224(1925); cf. *C. A.* 17, 1940.—The fibrous structure in strained metals is considered from the standpoint of 2 kinds of symmetry of the crystal arrangement: (1) a chosen lattice axis is in the direction of the fiber (linear rearrangement of axis); (2) the axis swings in a plane perpendicular to the fiber direction (plane rearrangement of axis), and the lattice rotates about the axis. The results on Cu and Al are as follows (type of strain, lattice axis rearranged in axial direction of test piece, state of rearrangement, kinds of symmetry, resp.): extension, [111], fairly regular, first kind; extension, [100], scattered, second kind with [011] in the lateral direction; compression, [110], scattered, second kind with [001] in the lateral direction; torsion, [111], scattered, second kind with [110] in the tangential direction. The effect of annealing Al after straining is shown qualitatively by photograpla. The strain pattern is practically entirely obliterated by annealing for 1 hr. at 600°. Cu retains the strain effect even at 1000°. The rearrangement likely to occur in a crystal aggregate by slip and rotation is assumed similar to that observed by Taylor and Elam (*C. A.* 19, 2287) for a single Al crystal. The theoretical consequences are in agreement with the exptl. symmetrical patterns. Reproductions of 32 X-ray pin-hole diagrams are excellent.

G. L. CLARK

X-ray diffraction effects from solid fatty acids. R. W. G. WYCKOFF, F. L. HURT AND H. E. MERWIN. *Science* 61, 613-4(1925).—Ordinary powder reflections as well as single-face reflections of large spacing are obtained from palmitic and other acids. Single specimens with all the optical properties of a true crystal and giving the same large-spacing X-ray reflections as solidified films on glass have been grown from soln. in acetone. There is as yet no X-ray evidence of the "smectic" state. Palmitic acid crystallizes in the monoclinic or triclinic system. The long C chains are not perpendicular to the face producing large spacings; hence exact information of the C-C distance is not possible, though variations from the perpendicular may be regular. Single plates give much more intense reflections than films on glass or mica, hence are promising for use as long-wave length gratings. Cf. Müller and Shearer, *C. A.* 18, 660; Piper and Grindley, *C. A.* 18, 3921; Gibbs, *C. A.* 19, 969; Trillat, *C. A.* 19, 2150; McBain, *C. A.* 18, 2093, 2827; Fridel, *C. A.* 19, 1072.

G. L. CLARK

Drying agents. J. H. YOE. *Chem. News* 130, 340-3(1925).—Brief critical review and comparative study of the more commonly used drying agents:  $P_2O_5$ ,  $Mg(ClO_4)_2$ ,  $Mg(ClO_4)_2 \cdot 3H_2O$ ,  $Al_2O_3$ ,  $H_2SO_4$ ,  $KOH$ ,  $NaOH$ ,  $CaO$ ,  $MgO$ ,  $CaCl_2$ ,  $CaBr_2$ ,  $ZnCl_2$ ,  $ZnBr_2$ . (Cf. Willard and Smith, *C. A.* 16, 3321; Johnson, *C. A.* 6, 2904; McPherson, *C. A.* 11, 2166; Marden and Elliott, *C. A.* 9, 1264; Fisher, Faust and Walden, *C. A.* 17, 41; Baxter and Starkweather, *C. A.* 10, 2838; Dover and Marden, *C. A.* 11, 2555; Baxter and Warten, *C. A.* 5, 1882.)

A. PAFINEAU-COCTURE

Viscosity measurements with glass. V. H. STOTT, EDITH IRVINE AND D. TURNER. *Proc. Roy. Soc. (London)* 108A, 154-71(1925).—Two app. are described for viscosity measurements of (1)  $10^{16}$  to  $10^4$  poises and (2) from  $10^4$  to  $10^2$  and less. In the former, the higher viscosities ( $10^{17}$  to  $10^9$ ) are calcd. from the angular velocity of a glass rod which twists under a known torque and the lower viscosities ( $10^3$  to  $10^2$ ) from the angular velocity of a rod of "reactol" plunged in the glass. In the latter, the rate of fall through the glass of a partially counterpoised Pt-Ir ball suspended from a wire of the same material was used to det. the viscosity. A furnace which will give a temp. const. to two or three degrees for an hour or two is described. Curves showing the temp.-viscosity relations for 13 (analyzed) glasses are given.

D. S. VILLARS

A boiling point relationship for molten salts. RICHARD LORENZ AND W. HERZ. *Z. anorg. allgem. Chem.* 141, 131-2(1925).— $T_b - \log T_s = 0.385$ , where  $T_b - 10$  is the abs. b. p. of the salt at 15 mm. pressure and  $T_s$  is the b. p. on the abs. scale at 760 mm. pressure. This quotient is very nearly const. for the considerable no. of salts enumerated. Marked deviations are noted only with  $Cu_2Cl_2$  (0.601),  $Cu_2Br_2$  (0.602),  $Cu_2I_2$  (0.613) and  $TlF$  (0.849). The deviation in the case of  $Cu_2I_2$  is attributed to a marked dissociation.

L. M. HENDERSON

Pressure-temperature charts for organic vapors. D. S. DAVIS. *Ind. Eng. Chem.*

17, 735-6(1925).—Cox's method (cf. C. A. 17, 2359) for plotting vapor-pressure data of hydrocarbons of the paraffin series may be applied to alcs., org. acids and some of the halogen-substituted benzenes. Curves are given for 5 alcs., 12 acids and 5 halogen derivs. of benzene. W. C. EBAUGH

Additivity of boiling points. J. J. VAN LAAR. *Physica* 5, 130-4(1925).—Objection is raised to the use of  $\sqrt{a}$  values calcd. from measurements of the b. p. (cf. van Arkel and de Boer, C. A. 19, 1361) instead of the crit. pt.; the b. p. is not a "corresponding" temp. and may give unreliable  $\sqrt{a}$  values. The use of  $\text{CH}_4$  and  $\text{CCl}_4$  values happens to be rather unfortunate since these substances show large discrepancies from the rules originally given. B. J. C. VAN DER HOEVEN

Additive properties of boiling points. II. A. E. VAN ARKEL AND J. H. DE BOER. *Physica* 5, 134-41(1925); cf. C. A. 19, 1361.—For many org. halogen compds., particularly Me halides, it is a sufficient condition for the additivity of the h. ps., that  $\sqrt{a_s}/b_s$  has the same value for every halogen; this leads to a b.-p. formula  $T_s = K(\Sigma V - V_s)/\Sigma V$  ( $= K_s(\Sigma \sqrt{a_s})/\Sigma V$ ) ( $V$  is the Kopp mol. vol.). If this equation is applied to ethane compds.  $K$  is found to have a lower value; this may be due to a mutual screening effect of the halogen atoms ( $X$ ) with a consequent decrease of  $\sqrt{a}$ . The authors express this effect in an empirical screening coeff. to be subtracted from  $\sqrt{a}$ . Values of the h. ps. of the pure halogens and of  $\text{ICl}$  and  $\text{IBr}$  calcd. in this manner agree well with the facts. B. J. C. VAN DER HOEVEN

A method for comparing the rates of mixing of two liquids. L. E. DODD. *Phys. Rev.* 22, 527(1923).—The method depends upon visual observation of the aberration, or scattering of light by striae present during mixing of a real and sharp light image. G. L. CLARK

Adsorption phenomena. II. Theories of adsorption. L. ARONNEN. *Rev. gén. sci.* 36, 262-8(1925); cf. C. A. 19, 1974.—A review. A. PAPINEAU-COUTURE

The adsorption of hydrogen and hydroxyl ions upon animal charcoal. C. KROETZ. *Biochem. Z.* 153, 173-84(1924).—The isoelec. point of charcoal is the  $p_H$  of that buffer mixt. which is not changed in reaction by addn. of the charcoal. This  $p_H = 7.58$ , and it is independent of the nature of the buffer and of the purity of the charcoal. Both strong acids and bases are partly neutralized by charcoal except near neutrality, when bases are no longer acted upon. W. D. LANGLEY

Research on base exchange with salts of organic nitrogen compounds. E. UNGERER. *Kolloid-Z.* 36, 228-35(1925).—There has been no agreement regarding the mechanism by which org. N compds. are held in soils. Some have considered them chemically bound; others consider them physically bound. This research was carried out to det. their condition. The absorbing or earthy material was a Ca permutite. It was prepd. by treating a K permutite with  $\text{CaCl}_2$ , and washing until the wash water was free from Cl. Its analysis was, loss by heating 20.65,  $\text{SiO}_2$  42.33,  $\text{Al}_2\text{O}_3$  25.53,  $\text{CaO}$  9.14,  $\text{K}_2\text{O}$  2.59%. Aq. solns. of guanidine-HCl, of betaine-HCl, of methylamine-HCl, of aniline-HCl, and of tetramethylammonium iodide; and alc. solns. of  $\text{NH}_4\text{Cl}$ , of cinchonine-HCl, of strychnine-HCl, and of quinine-HCl were used. When  $x$  = the no. of millimols of org. N compd. adsorbed,  $m$  = the mass of adsorbing permutite and  $c$  = the concn. of the soln., and  $\log x/m$  is plotted against  $\log c$ , the resulting curve is a straight line. This can be expressed by the formula  $x/m = kc^n$ . The value for the consts.  $k$  and  $n$ , resp., of this equation for the substances investigated are guanidine-HCl 1.070 and 0.734; betaine-HCl 0.794 and 0.486; aniline-HCl 0.210 and 0.245; methylamine-HCl 3.162 and 0.927; cinchonine-HCl 0.803 and 0.706; quinine, 0.616 and 0.710; and strychnine-HCl 1.122 and 0.710. The const.  $k$  is the adsorption coeff. The larger  $k$  is, the easier is the adsorption of the substance. The const.  $n$  is the adsorption exponent and is a measure of the curvature of the concn. curve. In most cases, when org. N compds. were adsorbed an equiv. amt. of Ca or K was found in the soln. In some cases, the sum of all equivs. in soln. after shaking with the permutite was greater than the equiv. of the org. N compd. before shaking. (When 5 g. of the permutite was shaken with 200 cc. of distd.  $\text{H}_2\text{O}$ , only 0.0002 g. of  $\text{CaO}$  was dissolved.) Ordinary unpurified clay acted very much as the permutite in adsorbing these substances. F. E. BROWN

The S-like adsorption curve. K. W. FLOROW. *Kolloid-Z.* 36, 215-7(1925).—The shape of an adsorption curve in its first part is dependent on the soly. of the adsorbent and that of the newly formed solid phase. If the adsorbent is less sol. the curve will be convex to the axis of abscissas; if the adsorbent is more sol. the curve will be concave to the axis of abscissas. The system  $\text{BaSO}_4 + \text{K}_2\text{CrO}_4 = \text{BaCrO}_4 + \text{K}_2\text{SO}_4$  was used to test this. Definite concns. and vols. of  $\text{K}_2\text{CrO}_4$  were added to weighed dry

samples of  $\text{BaSO}_4$ . The containers were sealed and shaken 3 times daily for 120 days and the supernatant liquid was titrated for  $\text{K}_2\text{CrO}_4$ . The adsorption per g. of  $\text{BaSO}_4$  was not proportional either to the vol. or to the concn. of the  $\text{K}_2\text{CrO}_4$  soln; nor was it inversely proportional to the mass of  $\text{BaSO}_4$  present. To explain this F. postulates a reaction  $2\text{BaSO}_4 + \text{K}_2\text{CrO}_4 = \text{BaSO}_4\text{BaCrO}_4 + \text{K}_2\text{SO}_4$  for the reaction in concd solns.

F. E. BROWN

**Adsorption. X. Adsorption of chrome alum by hide.** P. N. PAVLOV. *Kolloid-Z.* 36, 217-22(1925), cf. *C. A.* 19, 1924.—Because hide swells as it adsorbs a solute and takes up solvent also, the hide filings used in the first expts. were previously swollen with distd  $\text{H}_2\text{O}$  for 14 hrs. They were strongly pressed with filter paper. After pressing they contained 60%  $\text{H}_2\text{O}$ . When 8.25 g. of this hide was mixed with 74.57 cc. of chrome alum solns contg. from 0.9712 g. to 17.779 g. of  $\text{Cr}_2\text{O}_3$  per l., the adsorption was represented by the formula  $m_a/m = 4.13C^{0.814}$ , where  $m_a$  = the wt. of the adsorbed substance and  $m$  the mass of the adsorber. When 8.25 g. of this hide was mixed with 249.46 cc. of chrome alum soln contg. from 0.5875 to 17.779 g. of  $\text{Cr}_2\text{O}_3$  per l., the formula  $m_a/m = 2.193C^{0.847}$  expressed the adsorption. When 4.125 g. of this hide was mixed with 74.57 cc. of chrome alum soln contg. from 0.5875 g. to 17.779 g.  $\text{Cr}_2\text{O}_3$  per l. the equation  $m_a/m = 2.754C^{0.84}$  expressed the adsorption. The adsorption curves for these data are not the same and the adsorption is not proportional to the vol. of the soln nor inversely proportional to the mass of the adsorbent. The adsorption is a complex chem process (cf. *C. A.* 19, 760). Hide powder was prepd. as in the first expts. except it was merely drained, not pressed. Chrome alum was added and shaken for 24 hrs. at 14.5°. For 3 different ratios of wt. of hide powder to vol. of soln, the adsorption curves were nearly parallel but not coincident. This again indicates a complex chem process. Air-dried hide was similarly treated with chrome alum solns in varying ratios. In all cases there was a max. in the adsorption curve at low concns. and with increasing concns. the curves go into the range of negative adsorption. The chem process of hide reacting with Cr may be represented by the equations  $\text{K}_2\text{H}_2\text{O} + \text{CrX}_3 = \text{KCrX}_3 + 2\text{H}_2\text{O}$ ;  $\text{K}_2\text{H}_2\text{O} + \text{CrX}_3 = \text{KCrX}_3\text{OH} + \text{HX}$ ,  $\text{K}_2\text{H}_2\text{O} + \text{CrX}_3 = \text{KH}_2\text{X} + \text{CrX}_3\text{OH}$ , where K represents the active hide substance. Negative adsorption means merely that the solute and solvent are both adsorbed and the adsorption mixt. in the hide contains a higher percentage of solvent than the original soln.

F. E. BROWN

**The surface tension of clay slip.** W. OSTWALD AND W. RATH. *Kolloid-Z.* 36, 243-8(1925).—In some respects doughs and magmas such as clay slip are like solids, in others they are like liquids. Clay slip will pass through small tubes and form drops at the end of a tube as liquids do. The app. used to det. surface tension was a stalagmometer with tubes 0.5 cm. in diam. The tip from which the drops fell was enlarged on the outside and the bore almost closed at the tip. By means of a 3 way stopcock at the upper end of the tube, suction for drawing the slip into the tube, or pressure for causing it to flow out uniformly could be applied and regulated. The equations used were  $\sigma = k_1 g(1)$ ;  $g = dv(2)$ ;  $v = k_2 Z^{-1}(3)$ , where  $\sigma$  = surface tension,  $d$  = the density,  $v$  = the vol. of a drop and  $Z$  = the no. of drops in the vol. of the stalagmometer; and  $d = k_3 c(4)$ , if it is assumed that density is proportional to concn.  $c$ . From these  $\sigma = k_4 d Z^{-1}(5)$  or  $\sigma = k_5 c Z^{-1}$ . The rate of formation of drops was not given, and no correction was made for the shape of the drop. For 3 kinds of clay the drop nos. for all concns. decreased when subjected to mech. treatment. As the concn. of any clay is increased the drop no. increases to a max., when the concn. is between 15% and 20% and then decreases. These phenomena are explained by assuming a structure in the water-clay mixt. Deformation of this structure in the inner part of a body is opposed by viscosity, surface deformations are opposed by surface tension. Each increase in surface disturbs the optimum arrangement of particles.

F. E. BROWN

**A method of determination of the granulometric distribution of disperse systems.** RENE AUDUBERT AND HENRI RABATÉ. *Compt. rend.* 180, 1663-5(1925).—The method depends upon the pressure differences between 2 vertical tubes, suitably connected, during the process of sedimentation. Both tubes are filled with intergranular liquid and the disperse system is introduced into one.

G. L. CLARK

**Periodic deposition of magnesium hydroxide.** KATHARINA POPP. *Kolloid-Z.* 36, 208-15(1925).—Because  $\text{Mg}(\text{OH})_2$  forms sharp rings easy to count and measure, with a clear wide interspace and forms rings rapidly, it was selected for a qual. and quant. study of Liesegang ring formation. It is possible to put either the  $\text{MgCl}_2$  or the  $\text{NH}_4\text{OH}$  into the gelatin and pour the other on top but it is better to use the  $\text{MgCl}_2$  in the gelatin; for strong  $\text{MgCl}_2$  soln. (above 6 N) tears the gelatin. When a 1 or a 2 N soln. of  $\text{MgCl}_2$  is poured above a 3% gelatin gel contg. varying concns. of  $\text{NH}_4\text{OH}$ , the number of rings

increases with increasing concn. up to 0.60  $N$   $NH_4$ , after which it again decreases. Similar tests with gelatin and  $NH_4$  const. show an increasing number of rings with increasing concn. of  $MgCl_2$  up to 3  $N$ . Tests with 3 different proportions of  $NH_4$  and  $MgCl_2$  indicated that 3% gelatin sols were the best. The following facts were ascertained when  $MgCl_2$  was in the gelatin: (1) The no. and breadth of the rings increased and the interspace decreased in width with increasing concn. of  $MgCl_2$ , (2) the rings decreased in no. and width and the interspaces increased in width with the decrease in concn. of the  $NH_4OH$ ; (3) the rings increased in no. and width and the interspaces decreased in width with decreasing concn. of  $NH_4Cl$ , (4) with decreasing gelatin concn., the no. of rings remained the same but the width of both rings and interspaces increased; (5) the width of both rings and interspaces increased with decreasing temp.; (6) the rhythmic pptn. appears in gross, in colloidal, and in mol. particles. Similar ring formation occurs in agar, silicic acid gels, and even in fine sand filled with satd.  $MgCl_2$  soln. and in a satd.  $MgCl_2$  soln. Photographs of the tubes contg. the rings, drawings, and tables of data are given.

F. E. BROWN

**The stability of suspensions. I. The rate of sedimentation of kaolin suspensions by salts at varying hydrogen-ion concentrations.** WM. O. KERMACK AND WM. T. H. WILLIAMSON. *Proc. Roy. Soc. Edinburgh* 45, 59-70 (1925).—Both the concn. of the coagulating salt and the  $pH$  of the dispersion medium were varied systematically. Ten g. of com. kaolin was triturated with 0.03  $N$   $NH_4OH$ , let stand 24 hrs., and the supernatant liquid decanted. Repeating this 5 times removed particles less than 0.002 mm. in diam. The residue was stirred in 0.03  $N$   $NH_4OH$  and allowed to sediment 30 min., the supernatant suspension being employed for the expts. These suspensions contained 0.35 to 0.52 g. kaolin per 100 cc. and were shown by titration to contain 0.025  $N$   $NH_4OH$  with a  $pH$  between 9 and 10. One cc. did with an equal vol.  $H_2O$  cleared up only after 12 hrs. To 1-cc. portions of suspension were added 0.5 cc. of solns. of acids of varying concn. from 0 to 0.06  $N$  and 0.5 cc. of salt solns. of varying concn. The tubes were then shaken and readings of the sedimentation taken after periods of 5 to 15 min. by comparing the opacity of the supernatant liquid with the opacity of a series of standard comparison tubes contg. suspensions of varying amts. of  $BaSO_4$  in Na citrate solns. The  $pH$  of the supernatant liquid was measured. In nearly all cases increase in H-ion concn. favors sedimentation.  $NaCl$  increases the rate of sedimentation in alk. soln. but retards it in acid soln.  $KCl$  increases sedimentation at all values of  $pH$ .  $Na_2SO_4$  has little influence.  $Na_2HPO_4$  and Na citrate tend to maintain stability.  $CaCl_2$  and  $CaSO_4$  flocculate much more rapidly than any of the Na salts.  $CaH_2(PO_4)_2$  in concn. greater than 0.00  $N$  brings about a condition in which increasing acidity tends to stabilize the suspension. This is probably due to the formation of a ppt. of basic Ca phosphate on the surface of fine kaolin particles.  $AlCl_3$ ,  $FeCl_3$ , and  $LaCl_3$  have slight influence in acid soln., presumably because the H ion alone is a very effective coagulant. In alk. soln. the sedimenting effect with these salts is practically zero except in the range of  $pH$  7 to 8, in which the metal hydroxide appears to ppt. on the surface of the kaolin particles. At  $pH$  values between 6 and 3 no pptn. takes place and the particles acquire a positive charge due to stabilization by the colloidal metal hydroxides.

F. L. B.

**Emulsions.** WM. SEIFRIZ. *J. Phys. Chem.* 29, 738-49 (1925); cf. C. A. 19, 2290. III. Double reversal of oil emulsions occasioned by the same electrolyte.—Double reversal with the same electrolyte is the rule for olive-oil emulsions stabilized with galactose and treated with  $NaOH$  or  $Ba(OH)_2$ . The  $OH$  ion is primarily responsible, since it is not occasioned by  $NaCl$  or  $BaCl_2$ . Double reversal in unstable petroleum oil emulsions is occasioned by  $NaOH$ ,  $Ba(OH)_2$ , and  $Th(NO_3)_3$ , but not by  $BaCl_2$  and  $NaCl$ . The action of  $Th(NO_3)_3$  precludes ascribing to the  $OH$  ion alone the responsibility for the double reversal of petroleum oil emulsions. IV. Multiple systems.—Readily reversible petroleum emulsions frequently consist of more than one type of system, as shown by photographs. The existence of such systems is attributed to impurity of one or the other of the liquids or to the presence of different stabilizers. V. The stabilization membrane.—In many instances the stabilization membrane of emulsions may be of mol. dimensions; but, in others, the membranes are definite morphological, at times microscopically visible, structures.

HARRY B. WEISER

**Emulsions.** O. LANGE. *Z. dent. Öl-Fett-Ind.* 45, 105-7, 121-2, 151-3, 162-4, 190-2 (1925).—A discussion of principles for the production of technically important emulsions under the following headings: (1) Sepn. of emulsions (2) Formation of emulsions. (3) Technical production and destruction App. Special part. (1) Technical sepn. of emulsions. (2) Technical production of emulsions. P. ESCHER

**The colloid chemistry of technical emulsions.** WM. CLAYTON. *Ind. Chemist* 1, 223-5 (1923).

E. H.

The development of colloid chemistry. W. D. BANCROFT. *J. Franklin Inst.* 199, 727-60(1925).

JEROME ALEXANDER

Colloids. MARCEL REMY. *La nature* 53, i, 134-6(1925).—A general description.

C. C. DAVIS.

The general building plan of matter in the colloidal state. I. The form and the chemical composition of dispersed particles in suspensoid solutions and precipitates. P. P. v VEIMARN. *Kolloid-Z.* 36, 237-40(1925).—The idea, that colloidal particles are composed of complex chem. compds., recently enunciated as new, has been used by V. for 18 years. About 20 references are given to confirm this. This idea had led to the following ideas regarding the precise form of colloids. (1) The particles of suspensoids are ultramicroscopic crystals, or aggregates of the finest ultramicroscopic crystals. (2) These aggregates may contain only one kind of crystals or more than one kind. (3) These crystals may grow in size and to various shapes, especially long needle-shape. (4) The aggregates will have a more or less rounded shape and be formed like a flake or a feather. The chem. nature of colloids is given under 12 heads: (1) When some substance  $X$  adsorbs some other substance  $Y$ , the compn. of the outer layers will be  $XY$ . If the crystals of  $X$  are large the proportion of  $Y$  will be negligible. (2) If the particles are progressively made smaller the value of  $Y$  increases and may become relatively large. (3) The cause of the sorption may be the same as the cause for the formation of complex compds., or it may be the formation of an insol. ppt. with the surface of the particle. (4) When the particles are very small so that the surface layer is the major part of the particle, one cannot draw a sharp line between the 2 classes mentioned in (3). (5) An aggregate of crystals in whose pores is the dispersion medium and all it carries will be yet more complex in nature than any single crystal. (6) The collection of crystals into aggregates changes the compn. (7) As the crystals grow large the amt. of enclosed material decreases and the crystals become relatively purer. (8) As the concn. of the "Dispersator"  $D$  increases,  $\Delta$  in the formula  $XD\Delta$  increases. (When equal vols. of  $BaCl_2$ , ( $a + X$ ) normal, and  $MnSO_4$ , " $a$ " normal, are mixed,  $BaCl_2$  is the "Dispersator.") When the excess of  $BaCl_2$ ,  $X$ , is plotted against the life of the resulting colloid there is a max. life for mixts. for each value of  $a$ . On the 2 sides of each curve will be pairs of points representing colloidal particles of the same life period but of different compns. (9) Purifying colloidal particles by dialysis or any other method removes the "Dispersator," changes the compn., and makes any analysis futile. (10) Sizes of particles and compn. are changing continually. (11) and (12) As the particles grow,  $XY\Delta \rightarrow XY_e \rightarrow X$ , or  $\lim (XY\Delta)_\infty = XY_e = X$ . It is useless to talk of pure phys. or pure chem. theories. The theory is physicochem. F. E. B.

Preparation and properties of some protected silver sols. I. D. GARARD and G. E. DUCKERS. *J. Am. Chem. Soc.* 47, 692-6(1925).—A Ag sol can be prept. by heating a dispersion of AgOH contg. gum arabic, or by allowing the mixt. to stand. The properties of this sol were studied.

F. P. WIGHTMAN

Vanadium pentoxide sol. I. Streaming anisotropy. H. FRIEDRICH, F. STAPFEL-FELDT and H. ZOCHER. *Z. physik. Chem.* 114, 161-89(1924); cf. C. A. 15, 3578; 17, 3276.—The double refraction and dichroism (together called streaming anisotropy), which occur on the streaming of  $V_2O_5$  sol, have been quantitatively studied, and the influence of age and concn. of sol, of the velocity of flow, and the temp. has been det. The sol flowed through a tube with rectangular cross-section, and a polarization spectrometer with a half-shadow app. was employed for the measurements. The source of illumination was the green light of the Hg lamp. It was found that the anisotropy is strongly influenced by the age of the sol. In a freshly prepd. sol it is zero; it increases continuously with time, and finally reaches a max. The velocity of aging, at const. streaming velocity and temp., is given by the equations  $d\Delta/dt = k\Delta(\Delta_\infty - \Delta)^2$  and  $d\Gamma/dt = k\Gamma(\Gamma_\infty - \Gamma)^2$ , where  $\Delta$  is double refraction and  $\Gamma$  dichroism. The magnitude of the velocity of aging is very sensitive to the presence of impurities, arising from the  $NH_4$  vanadate used for the prepn. of the sol. The influence of arsenic acid is especially marked. The relation between the velocity coeffs. and the temp. is given by the Arrhenius equation  $\log k = -A/T + B$  in which the consts.  $A$  have values of over 10,000, and the temp. coeff. for  $10^\circ$  is about 4. If a sol which has reached the limiting value is diluted the anisotropy at first decreases in proportion to the diln. The rate of decrease then slowly diminishes, and finally a new limiting value is reached. This behavior probably depends on the fact that some of the colloid particles, which cause the double refraction, are in a state of true soln. The anisotropy increases with the velocity of flow. With fresh sols, the increase is regular, but with old sols, a limiting value is reached. For the same sol at different ages, a series of curves is obtained. A similar series is obtained if the aging is followed at a different temp. and concn., or with another sample of the starting

material ( $\text{NH}_4$  vanadate), or even with a different method of prepn. of the sol. With rising temp., the anisotropy diminishes, the influence of temp. being practically linear, and greater for fresh sols than for old. The double refraction of the sol corresponds, within the limits of error, to that of the  $\text{V}_2\text{O}_5$  contained in it. The abs. value of the double refraction is 1.7. II. The vortex cross. *Ibid* 190-207.—An investigation of the so-called vortex cross of  $\text{V}_2\text{O}_5$  sol, which is formed when the sol is rotated between 2 cylindrical walls and observed between crossed Nicols. Four minima of brightness are to be seen, giving the appearance of a dark cross, of which the arms form with the direction of polarization an angle depending on the exptl. conditions. The angle has been measured, and found to be independent of the thickness of the liquid layer and the concn. of the sol. It increases rapidly with increasing velocity gradient and increasing age of the sol, and decreases with rise of temp. The increase of the vortex angle  $\psi$  with age has been followed, and it is found that the velocity of aging is given by the equation  $d\psi/dt = k\psi(\psi_\infty - \psi)^2$ . The angle measured in the slowly changing fresh sol has the value  $45^\circ$ , while  $\psi_\infty$  approximates to  $90^\circ$ . If the increase of  $\psi_\infty$  with temp. is considered, the influence of temp. on the growth of the angle with age is given by the Arrhenius equation. The temp. coeff. for  $10^\circ$  is about 2.3. The behavior of the vortex cross is best explained in terms of the elasticity of the sol. The elastic deformation of the sol elements is small in fresh sols, and with small velocity gradient (cf. Schwedoff, *J. Phys.* [3] 1, 49 (1892)). It behaves like that of a rigid body, and the cross angle is  $45^\circ$ . When the velocity gradient is great, and as the sol ages, it approaches  $90^\circ$ . According to this, the cross angle is identical with the angle of max. deformation; and the direction of max. deformation corresponds with the direction of the velocity gradient. The colloid particles do not, therefore, arrange themselves along the stream lines, because of the friction between adjacent liquid layers of different velocities, but place themselves in the direction of max. deformation. Only in old sols and with high velocity gradients does this direction practically coincide with the direction of flow. B. C. A.

Studies in swelling. I. The swelling of agar-agar gels as a function of water content before swelling. B. L. CLARKE. *J. Am. Chem. Soc.* 47, 1954-8 (1925).—Starting with an agar contg. 1 g.  $\text{H}_2\text{O}$  per g. of dry agar, the % swelling in pure  $\text{H}_2\text{O}$  gives a curve which is practically a straight line up to 0.554 g.  $\text{H}_2\text{O}$  (415% swelling); at this point the curve changes its slope and rises sharply to a max. (0.313 g.  $\text{H}_2\text{O}$ , 3903% swelling), after which swelling capacity decreases somewhat more gradually with diminishing  $\text{H}_2\text{O}$  content, down to a 0 value for the latter variable (783-839% swelling). Agar gels, when freshly cast, are opaque; during the drying of these gels down to thin plates, this opacity changed rather sharply to perfect transparency at about 0.554 g.  $\text{H}_2\text{O}$ ; this may provisionally be associated with a change in phase. It is probable that there are other variable factors concerned in the detn. of the swelling capacity of an agar gel. C. J. WEST

Adsorption and osmosis in gels. T. TOMITA. *Biochem. Z.* 153, 335-57 (1924).—The surface tension, swelling, adsorption, and osmosis in gels contg. such  $\text{H}_2\text{O}$ -sol. or surface-active compds. as gelatin, albumin, agar, Na cholate, silicic acid and lecithin are observed, as well as the changes upon the properties named as affected by fatty acids, alics., urethan,  $\text{Et}_3\text{NH}$ , and solns. of these compds. in the presence of salts and suspensions. W. D. LANGLEY

Lipoid theory and surface activity theory. I. TRAUBE. *Biochem. Z.* 153, 358-61 (1924); cf. preceding abstr.—Both the lipoid theory and the surface-activity theory of osmosis are applicable, depending upon the nature of the system observed. W. D. L.

The action of salts with multivalent cations on colloidal solutions of gold and gum benzoïn. WM. O. KERMAK AND C. I. B. VOGEL. *Proc. Roy. Soc. Edinburgh* 45, 90-101 (1925).—The colloidal gum benzoïn was made by adding the alc. soln. to  $\text{H}_2\text{O}$ . The Au was made by the  $\text{CH}_3\text{O}$  method. The  $p_H$  in each case was varied by adding acid or alkali and then varying amts. of the salts were added.  $\text{CaCl}_2$ ,  $\text{BaSO}_4$ ,  $\text{FeCl}_3$ ,  $\text{AlCl}_3$ , and  $\text{LaCl}_3$  were employed with each of the colloids. Salts of trivalent cations are able to confer, under appropriate conditions of concn. and  $p_H$ , a positive charge on the particles of a negatively charged colloidal sol. Sepg. the region where the sol particles are positively charged from the region where they are negatively charged is a zone of pptn. These zones are closely related to the degrees of hydrolysis of the salts. The zone of positive charge may be due to the existence of a mol. of metallic hydroxide which is able to establish itself on the surface between the sol particles and  $\text{H}_2\text{O}$ , and to associate itself with a metallic ion. No such phenomena have been observed with bivalent ions. F. L. BROWNE

The influence of gelatin on the stability of a colloidal solution of cholesterol, and on the charge on the particles. WM. O. KERMAK AND PETER MACCALLUM. *Proc.*

*Roy Soc Edinburgh* 45, 71-89(1925).—Five cc of a 1% soln. of com. cholesterol in abs. alc. was added to 80 cc  $H_2O$  at  $65^\circ$ . The vol. was made up to 100 cc. with  $H_2O$  and the milk-like sol filtered through paper. The particles are about  $200\mu$  in diam and negatively charged. Pure cholesterol will not give a stable sol. Addn of Na taurocholate to pure cholesterol produced a stable sol. NaCl or acids ppt. the sol, the amt of coagulant required increasing as the concn. of the sol is decreased. Less NaCl is required for pptn in acid than in alk. soln. High concn. of NaOH also coagulates the sol. The cholesterol sol was added to sols or gelatin of varying concn. and of varying  $pH$  (obtained by adding acid to isoelec. gelatin sols). At  $pH$  4.5 complete pptn. of the cholesterol sol takes place in the region between gelatin concns. of 1/40,000 to 1/640,000. At  $pH$  3.5 the zone of gelatin concn. for pptn. is 1/160,000 to 1/2,560,000. At  $pH$  3.2 pptn. takes place unless the gelatin concn. is greater than 1/320,000. At  $pH$  2.8 concn. of gelatin of 1/640,000 is sufficient to prevent pptn. by acid. This zone of pptn. of the cholesterol seps. 2 zones of stable sols, the one having the relatively high concns. of gelatin contg. positively charged particles and the other negative. The p. d. between the particles and the medium in the mixed sols was detd. by cataphoresis, the U-tube method being used. In the region of  $pH$  from 5.5 to 11 the p. d. is roughly  $-25$  mv. In the region of  $pH$  from 4.5 to 1.5 the p. d. is roughly  $+14$  mv. When NaCl is added to the gelatin-cholesterol mixts. the zone of pptn. is widened. The results are explained on the theory that gelatin protects cholesterol sols when present in sufficient amt. to form monomol. layers at the interfaces between the particles and the medium. Pptn. takes place when enough gelatin is present at the interface to neutralize the charge on the cholesterol particles but not enough completely to cover the interfaces. F. L. B.

The kinetics of swelling and shrinking of gels. I. S. LIEFAROV, *Kolloid. Z.* 36, 222-3(1925).—The equation  $K = (1/t) \ln [m/(m-q)]$  (1), where  $m$  is the max. swelling and  $q$  the swelling at the time  $t$ , and the equation  $yK = (1/t) \ln [m/(m-QY)]$  (2), where  $Y$  is the velocity const. for any accompanying secondary reaction, were tested to det. their applicability to swelling and shrinking of gels. Glue and water and glue with each of the following sols: 0.025 N KOH, 0.025 N HCl, 0.025 N  $K_2Cr_2O_7$ , and 0.025 N  $K_4Fe(CN)_6$  were used. When  $H_2O$  and glue were used  $K$  from equation (1) was almost const. from  $t = 5$  min. to  $t = 25$  min., during which time 1.0856 g. of glue took up 1.8067 g.  $H_2O$ . When glue and any of the sols were used,  $K$  increased suddenly with increasing time but  $yK$  of equation (2) remained almost const. Formula (2) applies in all cases of swelling. Instead of shrinking the gel over  $H_2SO_4$  it was dehydrated in alc. Changing EtOH during the dehydration was less important than the choice of the original concn. of EtOH. The formulas  $K = (1/(a-E)) \ln [(a-Z)E/(E-Z)a]$  (3) and  $yK = (1/(a-E)) \ln [(a-YZ)E/(E-YZ)a]$  (4), where  $a$  is the original  $H_2O$  content of the gel,  $E$  is the mass of  $H_2O$  which the gel is able to give up, and  $Z$  the mass of  $H_2O$  given up in  $t$  sec., were tested for dehydration of gels. Equation (4) satisfactorily represents the dehydration of any known gel. F. E. BROWN

Aldehyde-sulfoxylates as protective colloids. XIV. Sulfoxyl compounds. A. BINZ AND H. BAUSCH, *Ber* 58B, 987-90(1925).—From an aq. soln. of Ag-arsphenamine,  $CO_2$  brings down a brown ppt. If formaldehyde-sulfoxylate is present, the pptn. does not occur. Neoarsphenamine, formed by condensation of formaldehyde-sulfoxylate with 3,3'-diamino-4,4'-dihydroxyarsenobenzene, also prevents the pptn. of Ag-arsphenamine by  $CO_2$ . The 2 components can be sepd. by ultrafiltration. Colloidal sols. of Cu. Ag. and Hg may be made with the help of neoarsphenamine. Aniline forms a colloidal soln. in  $H_2O$  in the presence of formaldehyde-sulfoxylate. R. J. HAVIGHURST

Electrodialysis. C. DUBAË, *Biochem. Z.* 153, 504-5(1924).—D. emphasizes his priority in the development of this method for the purification of colloids. Cf. *Compt. rend.* 140, 144(1905).

Electrocapillary analysis of colored colloids. W. KOPACZEWSKI, *Compt. rend.* 180, 1530-2(1925).—The expts. were made with colloids previously dialyzed, then fixed as to their elec. cond., surface tension and viscosity (cf. *Pratique des colloides* Paris 1923). Strips of filter paper 1 by 25 cm. cut from the same sheet were hung so that their lower ends were below the surface of the prepd. colloidal sols. and the rapidity of ascent of the different colors was noted. All of the colloidal colors were of 0.1% concn. with viscosities and surface tensions equal to that of  $H_2O$ . Their elec. resistances ranged between 10,000 and 35,000 ohms ( $H_2O$  6000 ohms). The results showed that the ascension of electrolytes in the strips of filter paper is not conditioned upon their elec. charges. Electropositive colors show at times a greater ascension in the strip than electronegative colors. Electronegative colloids show the same ascension as distd.  $H_2O$ , and the upper zone is generally strongly colored. Electropositive colloids ascend but very little. Amphoteric colloids show no regularity in their electrocapillary as-

cension, this ascension being accompanied with changes of color as if H and OH ions were produced. From the above-mentioned facts a rapid and sensitive method for the qual. analysis of colloidal dyes may be devised. A drop of the colloidal material on filter paper shows by the image formed whether the material is positive, negative or amphoteric.

L. W. RIGGS

The viscosity and elasticity of soap solutions. Preliminary communication. H. FREUNDLICH AND H. J. KORES *Kolloid Z.* 36, 241-3 (1925).—Sols. of Na oleate show no elasticity. Their viscosity  $R$  follows the basic equation  $R = Ndc/dr$ . Though coned sols. of Na stearate show some elasticity, dil. sols. do not. Tables of data for 0.54% Na oleate and 0.1% Na stearate show that these substances separately have low viscosities and no elasticity. When a soln. which contained, at the same time, 0.54% Na oleate and 0.1% Na stearate was investigated, the viscosity was from 6-fold to 40-fold that of a soln. contg. either alone. The behavior of the mixed soln. was similar to that of elastic sols. Under the ultramicroscope long threads could be detected in the mixed soln. They were not present in either soln. before mixing.

F. E. BROWN

The mutual solubility of liquids. J. A. V. BUTLER. *Chemistry & Industry* 44, 577-9 (1925).—Review of recent work, particularly in appreciation of the Hildebrand book "Solubility" (New York, 1924).

G. L. CLARK

Solubility of chlorine in carbon tetrachloride. G. M. SCHWAB AND G. HANKE. *Z. physik. Chem.* 114, 251-6 (1924).—The soly. coeff.  $s$ , has been detd. by measuring the decrease in pressure with time of Cl in an app. of known vol. connected with a very small flask contg. a small quantity of  $CCl_4$ . The value of  $s$  is found to be  $0.031 \pm 0.003$  at  $19^\circ$ . The "invasion" coeff., which is defined as "the no. of mols. which pass per second through 1 sq. cm. of surface with 1 atm. difference between the pressure in the gas phase and the osmotic pressure in the soln." is also detd. and is given as  $10^4 s = 2.2 \pm 0.5$  at  $19^\circ$ .

B. C. A.

The solubility curves of zinc sulfate. ERNST COHEN AND C. W. G. HETTERSCHJ. *Z. physik. Chem.* 115, 440-3 (1925).—The soly. of  $ZnSO_4$  in  $H_2O$  was detd. over a temp. range from  $0^\circ$  to  $55^\circ$ . The transition point of the hepta- to the hexahydrate was  $37.9^\circ$ .

ARTHUR GROLLMAN

Solubility of the crystalline hydrates of nickel sulfate. N. V. TANTZOV. *J. Russ. Phys.-Chem. Soc.* 55, 335-41 (1924).—The redetn. of solubilities was made to permit calcg. the temp. coeffs. of the soly. of the hydrates (cf. following abstr.). The green hexahydrate was obtained by rapidly cooling or shaking a supersatd. soln. of  $NiSO_4$ , the blue hexahydrate by passing a weak elec. current through a supersatd. soln. This causes the appearance of blue crystals on the Ni plated anode soon after the appearance of the green crystals, and upon the cessation of the current there is a continued growth of the blue crystals and the disappearance of the green crystals. Blue crystals so obtained have also been used for inoculations. Heptahydrate could never be made to form in such a way. Results of soly. detns. in terms of parts  $NiSO_4$  in 100 parts water:  $NiSO_4 \cdot 7H_2O$ :  $20^\circ$ , 37.70;  $25^\circ$ , 40.40;  $30^\circ$ , 43.28;  $35^\circ$ , 47.03;  $40^\circ$ , 50.42. Blue  $NiSO_4 \cdot 6H_2O$ :  $20^\circ$ , 40.09;  $25^\circ$ , 41.56;  $30^\circ$ , 43.56;  $35^\circ$ , 45.58;  $40^\circ$ , 47.60. Green  $NiSO_4 \cdot 6H_2O$ :  $20^\circ$ , 44.37;  $25^\circ$ , 45.30;  $30^\circ$ , 46.56;  $35^\circ$ , 47.76;  $40^\circ$ , 49.16. The temp. coeffs. of solubilities are: heptahydrate  $ds/dt = 0.67$ ; blue hexahydrate,  $ds/dt = 0.49$ ; green hexahydrate,  $ds/dt = 0.24$ , all at  $20^\circ$ . Transition points, heptahydrate  $\rightleftharpoons$  blue hexahydrate at  $31.55^\circ$ ; heptahydrate  $\rightleftharpoons$  green hexahydrate at  $36.7^\circ$ .

W. M. STERNBERG

The direction of spontaneous crystallization and chemical transformations. N. V. TANTZOV. *J. Russ. Phys.-Chem. Soc.* 55, 342-67 (1924).—An unstable system selects such a path of transformation that entropy changes are the least. For that reason where 2 cryst. forms may appear from supersatd. solns. the one having the lesser temp. coeff. is the more likely to be formed. When one cryst. form can change into another one the change takes place most readily at the transformation point where entropy changes are the least. In view of the proportionality between changes in entropy and changes in temp. coeffs. of vapor pressures and of solubilities the rule may be given in a more general form: of all possible changes in metastable systems the first one to take place is the one associated with the least changes of temp. coeffs. of vapor pressure and of soly. Thus S (trans. pt.  $96.5^\circ$ ) has been made to crystallize at various temps. from  $100^\circ$  down to  $80^\circ$  and  $60^\circ$ . The monoclinic S was always formed first, except when the melt was inoculated with crystals of rhombic S. The formation of the monoclinic form at  $100^\circ$  contradicts Ostwald-Bancroft's rule, but is in agreement with T.'s. Crystn. of hydrated  $ZnSO_4$ ,  $NiSO_4$ , and  $CuSO_4$  was studied by causing the beginning of crystn. by a new method, namely by passing a weak current through the soln. between an anode of Pt coated with the metal of the salt and a Pt-wire cathode. Crystns. at temps. above and below the transformation points  $ZnSO_4 \cdot 7H_2O \rightleftharpoons ZnSO_4 \cdot 6H_2O$  ( $39^\circ$ ) and of hydrated

$\text{NiSO}_4$  (cf. preceding abstr.) showed the first appearance of the form having the lower temp. coeff. of soly. ( $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ ; green  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ). A similar rule holds to det. the one chem. reaction to occur where many are possible; of all possible chem. transformations the one having the least temp. coeff. will occur first. W. M. STERNBERG

An investigation of the solubility of magnesium hydroxide. I. The existence of different modifications of magnesium hydroxide. J. K. GJALDRAEK. *Z. anorg. allgem. Chem.* 144, 145-68(1924).—The lack of agreement in the results of various workers on the soly. of  $\text{Mg}(\text{OH})_2$  led G. to undertake this study with the idea of detg. whether several modifications of  $\text{Mg}(\text{OH})_2$  exist, whether they show the same max. and min. values for soly., and how the change from one modification to the other takes place. Soly. detns. were made by means of cond. measurements with a  $\text{H}_2$  electrode, care being taken to exclude  $\text{CO}_2$ .  $\text{MgCl}_2$  soln. of different strengths was pptd. with  $\text{NaOH}$  and cond. measured over a long period. Instead of attaining a const. value, the potential continued to fall even after 144 days. G. explains this as due to reaction between the glass and the soln. with the formation of  $\text{Mg}$  silicate. On paraffining the glass this is eliminated. Where the quantity of  $\text{Mg}(\text{OH})_2$  pptd. was greater the fall of potential was more rapid, indicating that the transformation from the unstable to the stable form is more rapid with greater quantity of ppt. The presence of these 2 forms is also indicated by the reaction between  $\text{Mg}$  and  $\text{H}_2\text{O}$ , and by the hydration of  $\text{MgO}$ . The highest and lowest values obtained for the potential in all these reactions are given in a table. There is no good agreement in the highest values corresponding to the unstable form, probably because the change is too rapid at first, but there is very good agreement in the lowest values, representing the stable form, for the same concn. of  $\text{MgCl}_2$ , except where this becomes very low, of the order of 0.0008 mole  $\text{MgCl}_2$ . This indicates that in the transformation of the unstable  $\text{Mg}(\text{OH})_2$  first formed, a definite modification of  $\text{Mg}(\text{OH})_2$  with well-defined soly. is formed. This is supported by the fact that the soly. product for stable  $\text{Mg}(\text{OH})_2$  shows a good agreement over the entire range of  $\text{Mg}$ -ion concn. II. The solubility product and the dissociation constant of magnesium hydroxide. *Ibid.* 269-88.—Data reported in I. in addition to new measurements, are used as a basis for the calcn. in this paper. The soly. product,  $L$ , of  $\text{Mg}(\text{OH})_2$  is defined by the equation  $(\text{Mg}^{++})(\text{OH}^-)^2 = L$ , or  $[\text{Mg}^{++}][\text{Mg}^{++}(\text{OH}^-)^2] = L$ , in which ( ) indicates the activity and [ ] the concn. of the ions enclosed, and  $f$  the activity coeff. This is obtained as follows:  $-\log f = n.k\sqrt{C_{\text{ion}}}$ , where  $n$  = valence of the ions,  $k$  a const., and  $C_{\text{ion}}$  the ion concn. expressed in terms of normality. From these equations the following expression is derived:  $\log L = 2 \log (\text{OH}^-) + \log [\text{Mg}^{++}] - [n.k\sqrt{C_{\text{ion}}}]$ . The values obtained at  $18^\circ$  for the stable and unstable modifications are  $10^{-18.1}$  and  $10^{-12.1}$ , resp.  $L$  for the unstable form is practically independent of temp., since its heat of soln. is extremely small, while  $L$  for the stable form increases with increase in temp., its log increasing at the rate of 0.006 per degree rise in temp. The heat of soln. of the stable form is -2200 calories, and this really represents the heat of transformation from the unstable to the stable form. The dissociation const. for  $\text{Mg}(\text{OH})_2$  soln. is about  $10^{-12.1}$ , and from this and the soly. product, the soly. of the stable form in  $\text{H}_2\text{O}$  at  $18^\circ$  is calcd. as  $1.61 \times 10^{-4}$ , and for the unstable form  $7.0 \times 10^{-4}$  per l. The lack of agreement between the values as found in the literature is explained as due probably either to contamination with silicate from the glass vessels used, or to a lack of information about the character of the material used, that is the proportion of stable and unstable modification present. H. STORREZ

Influence of pressure on the solubility of substances. V. System: naphthalene-tetrachloroethane. E. COHEN, WILHELMINA A. T. DE MEESTER AND A. L. TH. MOESVELD. *Proc. Acad. Sci. Amsterdam* 28, 108-18(1925).—See C. A. 19, 2155. H. G.

The composition of a constant-boiling solution of hydrogen bromide in water. D. T. EWING AND H. A. SHADDOCK. *J. Am. Chem. Soc.* 47, 1901-4(1925).—At 760 mm. the soln. b. at about  $125^\circ$  and contained  $47.8 \pm 0.03\%$   $\text{HBr}$ . A. W. FRANCIS

The effect of sodium hydroxide upon the surface tension of a solution of sodium nonylate. W. D. HARKINS AND G. L. CLARK. *J. Am. Chem. Soc.* 44, 1854-6(1925).—A 0.1  $M$  soln. of  $\text{Na}$  nonylate has the lowest surface tension thus far found for a dil. aq. soln. (20°). The addn. of 0.008  $M$   $\text{NaOH}$  more than doubles this value to 48.8 dynes per cm. Further addn. causes a linear decrease of the surface tension. G. L. CLARK

The system acetic acid-water. G. POVARIN AND V. MARKOV. *J. Russ. Phys.-Chem. Soc.* 55, 381-2(1924).—Preliminary communication. A table of b ps and compas. of vapor for different concns. of  $\text{AcOH}$ . W. M. STERNBERG

Why is ice from sea water sweet? CH. M. VAN DEVENTER. *Chem. Weekblad* 22, 282-4(1925).—The reason is that the system ice-concd. brine has a lower vapor tension

and is therefore more stable than the system salt-ice-dil brine. In detg. f. ps. of dil. solns. it is to be borne in mind that the temp. observed is the f. p. not of the original soln. but of a more concd. soln. left after the initial sepn. of ice. Instead of calcg. the correction or extrapolating the real f. p. it is safer to det. analytically the concn. of a sample drawn close to the thermometer bulb immediately after the reading. M. JACOBSEN

How much water remains liquid after the freezing of a dilute solution? CH. M. VAN DEVENTER. *Chem. Weekblad* 22, 234-5(1925).—The liquid fraction of water is  $t_1/t_2$ ,  $t_1$  being the first ice point or the true f. p. of the original soln.,  $t_2$  the second ice point or the true f. p. of the soln. left after the sepn. of some ice. MARY JACOBSEN

The freezing point of weak aldehyde solutions. T. P. GLADSTONE SHAW. *Can. Chem. Met.* 9, 141(1925).—By the Beckmann app. detns. of the f. p. of aldehyde solns. were made with the following results. 4.8% aldehyde, 2.5°; 8.8%, 5.0°; 13.5%, 7.8°; 18.6%, 11.2°; 22.5%, 14.0°; and 31.0%, 23.0°. W. C. EBAUGH

Solubilities of sulfur dioxide and ammonia in water. T. K. SHERWOOD. *Ind. Eng. Chem.* 17, 745-7(1925).—A series of tables and curves is given, made up from data in the literature, showing solubilities of  $\text{SO}_2$  and  $\text{NH}_3$  in  $\text{H}_2\text{O}$  at various temps and partial pressures. W. C. EBAUGH

Freezing points of very dilute solutions of electrolytes. FRANK HOVORKA AND W. H. RODRIGUEZ. *J. Am. Chem. Soc.* 47, 1614-24(1925).—The app. consists of 2 identical Dewar tubes, suitably shielded thermally. Each tube contained pure ice, and into one pure water was introduced and into the other the dil. soln. at its f. p. The soln. was removed and fresh soln. added several times until no ice was caused to melt. The terminals of a 14-junction Cu-constantin thermocouple were in the tubes. By a special potentiometer with Cu coils, which eliminated thermoelec. disturbances, the temp. difference could be read with a precision of about 0.00002°. Both the water and dil. soln. were agitated by a current of air whose vapor pressure was that of ice at 0°. For the 7 electrolytes, KCl, CsCl,  $\text{K}_2\text{SO}_4$ ,  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{MgSO}_4$ ,  $\text{CuSO}_4$ , and  $\text{La}_2(\text{SO}_4)_3$ , f. p. data between 0.01 and 0.001 M are in excellent agreement with values calcd. from the formula of Debye and Hückel (*C. A.* 17, 2665). JAMES M. BELL

Cryoscopic measurements with nitrobenzene. II. Variation of the molecular depression with water content. F. S. BROWN AND C. R. BURY. *J. Chem. Soc.* 125, 2219-26(1924); cf. *C. A.* 17, 3526.—The depression by several normal solutes of the f. p. of  $\text{PhNO}_2$  of varying degrees of dryness has been studied up to a concn. of 0.06 mol. per 100 g. of  $\text{PhNO}_2$ . The change of the mol. depression const. with  $\text{H}_2\text{O}$  content of the solvent has been confirmed, but the authors differ considerably from previous workers in their est. of the magnitude of this change. An equation in which concns. are expressed as mol. fractions has been found to represent the exptl. results with much greater accuracy than the Raoult-van't Hoff equation and to give a quant. explanation of the change in mol. depression const. This equation is  $\Delta t_o = kn_s/(n_s + n_1)$ , where  $n_s$  and  $n_1$  are the no. of mols. of solute and solvent, resp. E. P. WIGGAMAN

Cryoscopic measurements with nitrobenzene. III. Equilibrium in nitrobenzene solution. F. S. BROWN. *J. Chem. Soc.* 127, 345-8(1925).—The dissociation of naphthalene picrate and of naphthalene-trinitrotoluene in nitrobenzene has been studied by detg. the m. ps. of different systems, the equation relating the equil. const. to m. p. data having been derived in an earlier paper (cf. above). The equil. const. for the naphthalene-trinitrotoluene system was found equal to 0.464 and for the naphthalene picrate system equal to 0.228. The max. observed m. p. lowerings were 4.02° and 2.34°, resp. From these equilibria the free energy of formation of the picrate at approx. 3° is calcd. as 2083 cal. per mol., which agrees well with Brønsted's value obtained from c. m. f. data (cf. *C. A.* 6, 700). A. W. KENNEY

Viscometric neutralization of monoacids by alkalis. Comparison of alkali chlorates, bromates and nitrates. LOUIS-JACQUES SIMON. *Compt. rend.* 180, 1169-71(1925).—The viscosities of solns. of  $\text{HBrO}_3$  and  $\text{HNO}_3$  and their mixts. with NaOH and KOH were detd. in the temp. range 8-25° and the concn. range 0 to 2 N. These are compared with similar data for  $\text{HClO}_4$  previously published (cf. *C. A.* 19, 1079). The viscosities of mixts. of equimolal solns. of acid and bases give linear curves with a min. at the neutralization point where the salt soln. is half the concn. of the unmixed acid and base. The new data, however, do not bear out S.'s former conclusion (*C. A.* 18, 2452) that mols. of isomorphous substances modify the viscosity of water equally. C. M. BOURTON

The displacement of acids by diffusion. E. DEMOUSSY. *Compt. rend.* 180, 1498-500(1925); cf. *C. A.* 18, 1076.—With a given acid and given anion, the excess of the latter which diffuses (and is liberated) varies inversely as the rate of diffusion of the metallic cation. With a given salt, the excess of anion increases with the degree of ionization of

the acid. This is proved exp'tly. by studying mixts. of  $\text{HCO}_2\text{H}$  with  $\text{BaCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{AcOH}$  with  $\text{CaCl}_2$ ,  $\text{NaCl}$ ,  $\text{KCl}$ ; citric acid with  $\text{KCl}$ ; oxalic acid with  $\text{KCl}$ . Similar diffusion results are obtained with mixts. of salts and alkalis.

A. PAPINEAU COUTURE

**Preparation of conductivity water.** ISAAC BENICOWITZ AND H. T. HOTCHKISS, JR. *J. Phys. Chem.* 29, 705-12 (1925).—Discussion of theory of prepn. and description of a convenient still for large quantities of water of cond.  $0.06-0.07 \times 10^{-4}$ . Tap water is distd. from alk.  $\text{KMnO}_4$  into a second still, in which it is treated with pure air and redistd. with partial condensation so as continuously to collect the equiv. of the middle fraction in an ordinary distn.

B. H. CARROLL

**Electrical conductivity measurements in dilute methyl- and ethyl-alcoholic solution at 0°, 25° and 56°.** P. WALDEN, H. ULICH AND F. LAUN. *Z. physik. Chem.* 114, 275-96 (1924), cf. *C. A.* 18, 7.—The conductivities of tetraethylammonium picrate, tetramethylammonium chloride, diethylamine hydrochloride, isobutylamine-HCl, and the tetraethylammonium salt of trinitroresorcinol have been measured at 0°, 25° and 56° in MeOH and EtOH solns., down to very great dilns.—in 1 case, to 60,000 l. per mol. The authors describe a new form of cond. cell, and methods for the purification of the alcs., for which the values of  $\epsilon_{25}$  were found to be 0.15 and  $0.23 \times 10^{-4}$ , resp. Tables are given of the conductivities at round dilns., the values of  $\Lambda_\infty$  being obtained graphically by the square-root law.

B. C. A.

**Conductivity determinations in non-aqueous salt solutions.** P. WALDEN AND H. ULICH. *Z. physik. Chem.* 114, 297-319 (1924); cf. preceding abstr.—Cond. data for solns. of neutral uni-univalent salts in MeOH and EtOH,  $\text{NH}_4\text{OH}$ , nitromethane, and acetophenone, are considered with reference to (1) the relation between cond. and concn., (2) the change of limiting cond. with temp., and (3) the mobilities of the ions (in the case of MeOH and EtOH solns.). Conclusion: In non-aq. salt solns., as in aq., the region of dil. solns. is characterized by the validity of the cube-root formula at medium dilns., and of the square-root formula at high dilns., but, as with aq. solns., the law of mass action is not applicable. The region of dil. solns. in the solvents here considered begins at some hundred l. per mol., whereas with water it begins at from 20 to 50 l. per mol. It is shown that the numerous earlier measurements giving evidence for the validity of Ostwald's diln. law in non-aq. solns. cannot be regarded as trustworthy. It is pointed out that the Hertz theory of ionic mobility, although it does not appear to agree with that developed by Debye and Hückel (cf. *C. A.*, 18, 190), nevertheless gives almost identical values of  $\Lambda_\infty$ . It does not appear possible to decide experimentally between these 2 theories at the present time, and further theoretical investigation is necessary. New exp'tl. data are advanced in support of the law  $\Lambda_\infty \cdot \eta = \text{const.}$  Ionic mobilities in MeOH and EtOH are calcd. for temps. between 0° and 56°. It is found that although the simple ions, e. g.,  $\text{Cl}^-$  and  $\text{Na}^+$ , have a much higher speed in water than the polyatomic picric acid and tetraethylammonium ions, in org. media the mobility of these simple ions rapidly falls off, ultimately becoming smaller than that of the complex ions. This effect can probably be explained by increasing solvation with decreasing dissociation const. of the medium. It is also shown that isomeric org. cations do not move with equal speeds, and that the no., nature and symmetry of the substituents in the  $\text{NH}_4$  radical exercise a marked influence.

B. C. A.

**Electric conductivity method at high temperatures and its importance in the study of solid solutions.** P. SALDAU. *J. Russ. Phys.-Chem. Soc.* 55, 275-86 (1924); cf. *C. A.* 11, 1626.—When a chem. compd. is formed from the components of a solid soln. sharp maxima are found on the cond. isotherms at different temps. In certain cases the location of maxima varies with the temp. approaching simple at, proportions at some lower temp. From the similarity with isotherms of internal friction studied by N. S. Kurnakov and co-workers shifting maxima are explained by dissociations at higher temps. of the compds. formed. By plotting the curves of resistance of different samples through a range of temps. the transformation points appear as breaks on the curves similar to the retardation points on cooling curves. System  $\text{Au-Zn}$ —In the solid  $\alpha$  phase at about 420° a compd.  $\text{AuZn}$  is formed with the appearance of a new phase  $\alpha_1$ , which in turn undergoes at 270° a transformation with the formation of the second modification  $\alpha_2$ , stable at low temps.  $\text{AuZn}$  is stable at all temps. up to the m. p. The compd.  $\text{AuZn}_2$  found by Vogel does not exist. In the solid  $\gamma$  phase on cooling from 525°  $\text{AuZn}_2$  is formed, causing the appearance of two new solid phases,  $\gamma_1$  (520-250°) and  $\gamma_2$  below 250°. System  $\text{Au-Cd}$ — $\text{AuCd}$  is formed on cooling  $\alpha$  at about 450° with the appearance of two modifications  $\alpha_1$ , 450-135°, and  $\alpha_2$ , below 135°. The compd.  $\text{AuCd}_2$  reported by Vogel does not exist.  $\text{AuCd}$  is stable through temp. changes up to the m. p. and the existence of  $\text{AuCd}_2$  is substantiated.

W. M. STERNBERG

The mechanism of the process of dissociation in solution. C. J. BROCKMAN, *Chemistry and Industry* 44, 501-2(1925).—B presents the evidence against the generally accepted present-day view that the solute, not the solvent, produces the ions. Evidence is accumulating in favor of the view that the reverse is the case. E. G. R. ARDAGH

The basis for the physiological activity of certain onium compounds. The mobilities of the onium ions. I. Sulfonium ions. ISAAC BENICOWITZ AND R. R. RENSHAW, *J. Am. Chem. Soc.* 47, 1901-16(1925).—The mobilities of  $\text{Me}_3\text{S}^+$  and  $\text{Et}_3\text{S}^+$  ions were found to be 51.36 and 36.05, resp., at  $25^\circ$ . The mobilities of onium ions and their effect on potential of lipid-water interfaces are thought to have some relation to physiological activity. A. W. FRANCIS

Rate of decomposition of nitrogen pentoxide at low concentration. J. K. HUNT AND FARRINGTON DANIELS, *J. Am. Chem. Soc.* 47, 1602-9(1925).—This reaction which seems to be the sole survivor of unimol. reactions was investigated at low concns to det. whether there are differences in mechanism at high and low concns. The sp. reaction rate is independent of concn. even at partial pressures of  $\text{N}_2\text{O}_5$  as low as 0.01 mm. Hg. The presence of a large excess of N does not alter the rate. The reaction is not autocatalytic, for the reaction rate is unaltered even when the reaction approaches completion. JAMES M. BELL

The velocity of saponification of ionic esters. J. N. BRÖNSTED AND AGNES DELBANCO, *Z. anorg. allgem. Chem.* 144, 248-56(1925), cf. *C. A.* 16, 2056, 4113, 18, 1002. —According to the new theory of reaction velocity, the velocities of the 2 steps in the sapon. of an ester of a dibasic acid follow different laws. While the velocity const. of the first step (reaction between the electrically neutral ester and hydroxyl ion) should show at most only a linear dependence on concns. of base or neutral salt, the velocity const. of the second step (reaction between ionic ester and hydroxyl ion) should show an "exponential" positive neutral salt effect. The predicted behavior of the velocity in the first step has often been verified. To the study of the second step the sapon. of nitrourethane ion by NaOH is adapted because this reaction may be followed by measurement of the  $\text{N}_2\text{O}$  which is liberated by the immediate decompn. of the nitrocarbaminate ion. The velocity const. of this second step increases with increasing total ionic concn. and with increasing neutral salt content, as required by the theory. Increase of valence of the cation of the neutral salt has a marked effect, in accord with the principle of sp. interaction of ions (*C. A.* 16, 2037). The valence of the anion has little effect on the velocity const. The results are in good agreement with the new theory. R. J. HAVIGHURST

Reaction velocity of oxygen with solutions of some inorganic salts. III. The catalytic oxidation of sulfites. W. REMBERS AND S. I. VLES, *Rec. trav. chim.* 44, 249-68(1925); cf. *C. A.* 19, 1522-3.—Titoff's results (*Z. physik. Chem.* 45, 645(1903)) on the oxidation of sulfites are the most important on the subject and were confirmed and extended. T. found that the reaction velocity is monomol. with respect to the sulfite concn. but this const. decreased during the reaction. Within limits the  $\text{O}_2$  pressure or concn. has no effect on the velocity of the oxidation. Concns. of  $10^{-15}$  mol. per l. of Cu salts affect the reaction. Addn. of alkali or acid retards the reaction. The negative influence of glycerol, mannitol, etc., is solely due to a decrease in the concn. of the positive catalyst. Preliminary expts. showed that in a bisulfite soln ( $p_{\text{H}} \approx 3$ ) where  $\text{SO}_3$  ions have practically disappeared the oxidation velocity becomes immeasurably small regardless of the nature of the catalyst. Cupric and ferrous salts are active between  $p_{\text{H}}$  4 and 12 and reach an optimum somewhere in the interval.  $\text{Ni}^{++}$  and  $\text{Co}^{++}$  salts act catalytically only in alk. solns. where they are present as the hydroxides. In the presence of  $\text{NH}_3$  no oxidation is observed;  $\text{Cu}^{++}$  is fairly active;  $\text{Fe}^{+++}$  very little and the complexes of Co and Ni have no catalytic effect. The influence of  $p_{\text{H}}$  on the velocity of reaction in the absence of a catalyst shows the same character as with the addn. of  $\text{Cu}^{++}$  and  $\text{Fe}^{+++}$ , which agrees with T.'s belief that measurable oxidation is due to the presence of Cu and Fe salts. Detailed study of the catalysis of Cu salts in  $\text{NH}_4\text{OH}$  solns. showed that the reaction is monomol. in terms of sulfite concn., that  $\text{O}_2$  pressure has little influence; that the velocity of reaction decreases with increasing concn. of  $\text{NH}_4\text{OH}$ ; that the velocity is proportional to the concn. of the catalyst; and that the influence of temp. is normal. The oxidation of sulfites without and with a catalyst and with Cu salts as catalysts was studied in detail. Although it is impossible according to T. to obtain a sulfite soln. free from all positive or negative catalysts, comparable results were obtained by using the same sample of doubly distd. water for all purifications and expts. The reaction-velocity curve with respect to the  $p_{\text{H}}$  was traced and the optimum velocity was found to lie at  $p_{\text{H}} \approx 10$ . When KCN and glycerol were added as negative catalysts it was necessary to add more positive catalyst in order to

obtain measurable velocities. This was done by adding ordinary distd.  $H_2O$  to the special  $H_2O$ . The optimum for these systems is moved to a somewhat lower  $p_H$ . The results with Cu confirm those of T. Two constituents ( $SO_3$  and  $Cu^+$ ) det. the velocity const. and both are strongly dependent on the  $p_H$ . Lowering the  $p_H$  decreases the velocity because the  $SO_3$ -ion concn. decreases with the formation of  $HSO_3$  and  $H_2SO_3$  so that at  $p_H \approx 3$  scarcely any  $SO_3$  ions exist and the velocity is very small. On the other hand at  $p_H$  10 or 11 and upwards the concn. of  $Cu^{++}$  diminishes and the reaction is also retarded and when all  $Cu^{++}$  is converted into  $Cu(OH)_2$  the reaction is very slow. In the presence of KCN, glycerol, etc., feebly dissociated Cu-complexes are formed in which the  $Cu^{++}$  concn. is less than in the absence of the substance. T.'s interpretation of the reaction mechanism could not be adequately proved. In other publications results differing from those here given are recorded, which R. and V. attribute to less accurate methods of work. Ni and Co were also found to be active catalysts in alk. solns; the catalysis in this case must be ascribed to the hydroxides of Ni and Co and the mechanism has a close relation with induction phenomena which these hydroxides show with sulfite and  $O_2$ . On the basis of the data given the interpretation of Haber and Brann (*Z. physik. Chem.* 35, 84(1900)) is somewhat modified as follows: (a')  $Ni(OH)_2 + Na_2SO_3 = \text{complex (adsorption)}$ ; (a'')  $\text{complex} + O_2 \rightarrow Ni(OH)_2 + Na_2SO_4$ ; (b)  $2Ni(OH)_2 + Na_2SO_3 \rightarrow 2Ni(OH)_2 + Na_2SO_4 + H_2O$ . If reaction (a') and (b) are infinitely rapid compared with (a'') then the latter det. the rate of  $O_2$  absorption and is measured in the expts. The velocity is independent of the  $O_2$  pressure as was found to be true.

E. J. WITZEMANN

The thermal decomposition of silver carbonate. M. TRENTNERSIVER AND B. BRUYS. *J. Phys. Chem.* 29, 733-7(1925).—Whereas cryst.  $Ag_2CO_3$  shows a normal behavior on heating, i. e., it acts as a monomol reaction, the amorphous  $Ag_2CO_3$  behaves differently, reminding one of the rate of decay of radiation intensity of plates exposed for a short period of time to Ra emanation. The existence of an intermediate product, an unstable oxycarbonate, is therefore assumed. At const. temp. the velocity of decompn. decreases at first, then remains const. for a certain period, and finally decreases exponentially with time; in a certain interval of temp. (245-260°) the velocity of decompn. decreases with rise of temp.

W. C. EBAUGH

The rate of thermal decomposition of sulfuryl chloride. A first-order homogeneous gas reaction. D. F. SMITH. *J. Am. Chem. Soc.* 47, 1862-75(1925).—The rate of the reaction is independent of the glass surface and of the wave length of light. None of the theories for monomol. reactions agrees with both these results and those of the decompn. of  $N_2O_5$ , the other known example. A new app. for such expts. was devised.

A. W. FRANCIS

The activation of atoms and molecules. N. R. DHAR. *Z. anorg. allgem. Chem.* 141, 1-22(1924).—D. advances a no. of reasons and many data which support the view that atoms and mols. may exist in an active state. He indicates that the view is substantiated by the following observations: (1) that reactions between electrolytes are reversible and ionic reactions are more rapid than non-ionic reactions; (2) reactions of limited speed necessitate the assumption that only a portion of the mols. in the reacting system are in an active state; (3) the mols. in ordinary thermal reactions are activated by the absorption of infra-red radiation; (4) the temp. coeffs. of positive and negative catalyzers are in harmony with this view; (5) the phenomena of tautomerism and mutarotation; (6) the exptl. results of Wien, Milne and Weigert each indicate that the life of an active atom is approx.  $10^{-12}$  sec.; (7) the phosphorescence of Hg vapors observed by Phillips permits an explanation based on the concept of activation; (8)  $N_2$ ,  $O_2$ ,  $H_2$ , and  $Cl_2$  are activated by means of light or elec. discharge; (9) the origin of the light produced by slow oxidation of P may be traced to the formation of active O which gives off light upon reverting to the inactive form.

L. M. HENDERSON

A theory of the catalytic surface. H. S. TAYLOR. *Proc. Roy. Soc. (London)* 108A, 105-11(1925).—Langmuir's view that the surface of a catalyst is to be regarded as an area contg. a definite no. of elementary spaces in which some of the spaces are vacant, while others are covered with adsorbed atoms or mols. (cf. C. A. 16, 7) has been modified in such a way as to be more in accordance with the exptl. results obtained from investigations on contact catalysis, adsorption, heats of adsorption, catalyst poisoning, and X-ray exarns. of crystals. According to the new concept, a surface of a granule may be regarded as composed of atoms in varied degrees of satn. by neighboring atoms (detached to varying extents from the normal crystal lattice) varying from those 1 degree less satd. than interior atoms to those which are only held to the solid surface by a single constraint. It is by this constraint alone that these outermost atoms differ from gaseous metal atoms. The amt. of surface that is catalytically active is detd. by the

reaction catalyzed. There will be all extremes between the case in which all the atoms in the surface are active and that in which relatively few are active. R. L. DODGE

A study of catalytic actions at solid surfaces. XII. Some observations relative to those particles of a catalyst which participate in chemical change. E. F. ARMSTRONG AND T. P. HILPITCH *Proc. Roy. Soc. (London)* 108A, 111-20(1925).—Expts on the hydrogenation of whale oil in the presence of Ni catalysts and the toxic action of impurities are in accordance with the earlier concept of "active patches or particles" in the surface of the catalyst (cf. C. A. 16, 183). Taylor's concept of isolated or semi-isolated Ni atoms (cf. preceding abstr.) although in accord with most of the exptl. facts is not completely satisfactory because it is difficult to understand why a strongly exothermic reaction taking place on the catalyst surface should not result in a progressive devaluation of the catalyst in consequence of a series of localized exposures to high temps. This insufficiency of Taylor's concept can be overcome by regarding the acting atom of Ni as detached entirely from its association with the neighboring metallic atoms during the moment in which catalytic interchange is effected. Such an assumption accords with certain observations made on the hydrogenation and dehydrogenation of oils in the presence of Ni catalysts. R. L. DODGE

The catalytic decomposition of nitrous oxide on the surface of gold: a comparison with the homogeneous reaction. C. N. HINSHELWOOD AND C. R. PRICHARD. *Proc. Roy. Soc. (London)* 108A, 211-5(1925).—The rate of catalytic decomn. of  $N_2O$  on a gold-wire surface was measured at 200 mm. and 400 mm. initial pressure. The temps. of the gold wire were 834°, 938° and 990°. The rate was calcd. from the decrease in pressure in the system. The velocity consts. so obtained showed the reaction to progress in accordance with the simple uni-molecular law,  $-d(N_2O)/dt = k(N_2O)$ . This is in contrast to the earlier measurements of this reaction velocity in the absence of a catalyst, where the rate is given by the equation  $-d(N_2O)/dt = K(N_2O)^2$  and to the earlier measurements in the presence of a Pt catalyst where the rate was  $-d(N_2O)/dt = k(N_2O)/[1 + b(O_2)]$  (cf. C. A. 19, 429, 1805). The temp. coeff. of the reaction in the presence of the Au is given by the equation  $d \log k/dT = E/RT^2$ ;  $E = 29,000$  cal. per g. mol. R. L. DODGE

Catalytic decomposition of acetic acid by means of charcoal. N. V. KULYASHOV AND (Miss) N. A. KUDRYASHEVA. *J. Russ. Phys.-Chem. Soc.* 55, 383-96(1924).—Appreciable decomn. of vapors of AcOH in contact with charcoal could be detected at 300°, greatly increasing with the rise in temp. For the same temp. hydrous AcOH is less decomposed than the anhydrous. When anhydrous acid is used about half of it is decomposed into methane and acetone, while more than half is decomposed in the presence of water. Acetone is but little decomposed by charcoal at 400°, and still less so in the presence of water. A modification of Messinger's method for the detn. of acetone gives good results in the presence of AcOH: the AcOH is neutralized with normal KOH; then for each 10 cc. of the soln. contg. a total of 0.2-0.3 g. acetone, 25 cc.  $N$  KOH is added, after which 30-40 cc. 0.2  $N$   $I_2$ . The excess of KOH is next exactly neutralized with  $NH_4SO_4$ , the soln. allowed to stand  $\frac{1}{2}$  hr. the excess of  $I_2$  reduced with an excess of standard thiosulfate and the titration finished with  $I_2$ . W. M. S.

The anticatalytic action of hydrocyanic acid. OTTO WARBURG AND SHIGERU TODA. *Naturwissenschaften* 13, 442-3(1925).—The action of HCN as a poison for animal respiration due to inhibition of O transfer by Fe finds an analog in the purely inorg. anticatalysis by HCN of the oxidation of oxalic acid by iodic acid, for which the presence of traces of Fe (normal impurities) as catalyzer were found to be essential. B. J. C. VAN DER HOEVEN

Mechanism of the action of promoters in catalysis. M. C. BOSWELL AND C. H. BAYLEY. *J. Phys. Chem.* 29, 679-92(1925); cf. C. A. 19, 1367.—Metallic contact catalysts formed by reduction of oxides are considered to owe their activity to an adsorbed layer of dissociated water. Poisons eliminate this; promoters increase it.  $H_2$  remaining in Fe, Ni and Pt catalysts, presumably as water in this layer, is shown to be greater in the presence of promoters. B. H. CARROLL

Remarks on the work of A. Joffé and M. Lewitzky. The solid and elastic limits of natural rock salt. W. EWALD AND M. POLANYI. *Z. Physik* 31, 746-9(1925); cf. C. A. 19, 1799. H. C. U.

Equilibrium in solutions of the isomorphous salts,  $(NH_4)_2SO_4 \cdot MgSO_4 \cdot 6H_2O$  and  $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$ . I. ZWISLOCKA. *Roczniki Chem.* 4, 331-41(1924).—The solubilities of mixed crystals of these salts between 0° and 6° indicate that the double sulfates are miscible in all proportions and that, in chem. compn., the mixed crystals differ little from the soln., although the 2 component salts differ in soly. If  $c_1$  and  $c_2$  indicate, resp., the mol. concns. of the 2 double sulfates in the soln., and  $x_1$  and  $x_2$  the mol.

proportions of the 2 in the mixed crystals, the values of  $c_1/x_1$  and  $c_2/x_2$  are const; from this it is inferred that the crystal mol is identical with the simple chem mol B C A.

Physical equilibrium in the system acetic acid-acetic anhydride. G. POVARININ AND V. MARKOV. *J. Russ. Phys.-Chem. Soc.* 55, 375-80(1925).—Pure AcOH and Ac<sub>2</sub>O prep'd from it were used. The equil const  $k$  from 27 observations was found to be  $0.419 \pm 0.030$ , where  $\pm 0.030$  is the av. error. The compn. of the vapor and the boiling soln can be obtained from  $[x(100-y)]/[y(100-x)] = 0.419 \pm 0.039$ , where  $x$  and  $y$  are the % concns of the anhydride in the vapor and the liquid. In general the compn of the vapor is proportional to that of the liquid, no side reactions having been observed. The b. ps. of the mixts can be calcd. from the formula  $T = 118 + 22y$ , where  $y$  is the concn of the anhydride, 118 b. p. of the acid, and 22 the difference between the b. ps. of the anhydride (140°) and that of the acid. Tables are given of the compn of the liquid mixts and their vapors at the b. ps. of the mixts. W. M. STERNBERG

The equilibrium diagram of the system iron-carbon-titanium. KANZI TAMARU. *Sci. Repts. Tôhoku Imp. Univ.* 14, 25-32(1925).—Below 4% Ti forms solid solns with Fe-C. With more Ti the soly of C in the Fe-Ti eutectic decreases. Ti accelerates the graphitization of carbide. A. W. FRANCIS

The equilibrium relations for bismuth-cadmium and lead-antimony in the liquid and solid phases. V. FISCHER. *Z. tech. Physik* 6, 146-9(1925); cf. *C. A.* 19, 1684.—The thermodynamic potential is used to derive a formula for the equil relations of 2 metals. The results so calcd. for the 2 systems agree quite well with exptl data. J. H. PERRY

Displacement of metals from solutions of their salts by less electropositive elements. II. The reaction between amides of the alkali and alkaline earth metals and elements more electropositive than tin. F. W. BERGSTROM. *J. Am. Chem. Soc.* 47, 1836-41(1925), cf. *C. A.* 18, 2991.—A metal, such as Al, reacts with alkali amides, partly displacing the Na or K, which then reacts with the solvent, NH<sub>3</sub>, the final product being an ammonio salt analogous to aluminates in the H<sub>2</sub>O system. La and Ce salts have been made. A. W. FRANCIS

The mechanism of the fixation of nitrogen as sodium cyanide. E. W. GUERNSEY AND M. S. SHERMAN. *J. Am. Chem. Soc.* 47, 1932-40(1925).—Three reactions take place: (a) Na<sub>2</sub>CO<sub>3</sub> is reduced to Na, (b)  $2\text{Na} + 2\text{C} \rightarrow \text{Na}_2\text{C}_2$ ; (c)  $\text{Na}_2\text{C}_2 + \text{N}_2 \rightarrow 2\text{NaCN}$ . Only (c) is catalyzed by Fe. A. W. FRANCIS

Legal temperature—legal unit of heat. FRIEDRICH AUERBACH. *Z. angew. Chem.* 38, 447-9(1925), cf. Henning, *C. A.* 19, 2293.—The German legal units of energy are the kilowatt hour and the kilocalory, from 145° to 155°. The temp. is fixed legally by 10 melting, boiling and transformation points, 8 of which are actually used for standardization of thermometers (b. p. of O<sub>2</sub>, CO<sub>2</sub>, m. p. of Hg, H<sub>2</sub>O, b. p. of H<sub>2</sub>O, S, f. p. of Ag, m. p. of Au) in °. From -193 to +630.5° the Pt-resistance thermometer is prescribed and 2 interpolation formulas are given for the ranges below and above 0. From 630.5° to 1063° the thermoelement of Pt and Pt + 10% Rh has to be used, and above this the pyrometer, again with the interpolation formulas given. The limits of error for standard glass thermometers are given. J. T. STERN

The German law of Aug. 7, 1924, relating to temperature scale and heat unit. F. HENNING. *Naturwissenschaften* 13, 421-5(1925). B. J. C. VAN DER HORVEN

The specific heat of liquids according to the theory of corresponding states. R. FOA. *Atti accad. Torino* 60, 294(1924-5).—F proves, thermodynamically, that, for all fluids which follow the law of corresponding states, there is for each value of  $T^*$  (reduced temp.) the same value of the difference between the sp. heat referred to a mole of liquid along the limiting curve, and the sp. heat at const. pressure in the state of a perfect gas. A. W. CONTIERI

The measurement of the ratio of the specific heats using small volumes of gas—the ratios of the specific heats of air and of hydrogen at atmospheric pressure and at temperatures between 20° and 183°. J. H. BAINSWORTH. *Proc. Roy. Soc. (London)* 107A, 510-43(1925).—The adiabatic expansion method was used, giving  $\gamma$ , with bulbs from 600 cc to 11 cc, and a very fine Pt thermometer. With the 11-cc bulb the result was only 4% lower than with an enormously larger one (the difference being due to conduction of heat to the walls), and the final results were obtained by a linear extrapolation over only 1%, based on the values for different sized bulbs. The accuracy is estd. at 1 per mille, and agreement is generally better than 1% with the values of others. The error in the derived sp. heat is about 3 times that in  $\gamma$ . For air  $\gamma$  and the mol. heat at const. vol., resp., were at 290° 1.4032, 4.948; at 105° 1.4077, 4.937; at 155° 1.4154, 4.896. For H the values were at 290° 1.4070, 4.879, at 273° 1.4090, 4.844; at 252°

1.4203, 4.729; at  $195^{\circ}$  1.4127, 4.488; at  $155^{\circ}$  1.4800, 4.142; at  $90^{\circ}$  1.6054, 3.301.

W. P. WHITE

**Calorimetric researches. VIII. The paraffin oil method; an aid in the determination of the heats of combustion of difficultly combustible and hygroscopic substances.** P. E. VERKADE, J. COOPS AND H. HARTMAN. *Rec. trav. chim.* 44, 206-16 (1925); cf. *C. A.* 18, 2825, 19, 205.—The behavior of a great variety of org. compds. during combustion in the calorimetric bomb is considered. Many compds. could be burned in the form of pastilles without the addn. of any auxiliary substances and ignited with a cotton thread one end of which is placed under the pastille. In other cases ignition was obtained by soaking the thread in naphthalene. But many substances could not be completely burned by either of these methods even at  $O_2$  pressures of 35 atms. In cases of difficulty, complete combustion was obtained by placing a few drops of paraffin oil on the pastille (made as porous as possible). The oil-soaked pastille was then ignited by a slight modification of the cotton-thread technic. About 90 mg. of oil which develops about 1000 cal was used and the amt. used was accurately detd. by weighing. The thermal effect (Benetzungswärme) of wetting the compd. with the oil is not more than 1/5000 of the heat of combustion of C. The cases in which this oil method can be used in which the other methods fails follow: (1) substances with low heats of combustion, (2) substances with a high m. p., (3) substances that form a voluminous mass of crystals; (4) hygroscopic substances.

E. J. WITZEMANN

**The law of heat compression.** A. KOREVAAR. *Chem. Weekblad* 22, 230-5 (1925).—K. proposes a generally valid "law of heat compression." For  $t$ , temp. of preheated air ( $\times$  kg. per min.),  $T$ , temp. av. of the combustion zone (comprising oxidizing and reducing part) with a cylindrical outer surface  $O$  and an outside temp.  $T_0$ , this law can be expressed:  $kO(T - T_0) = x(407 + 0.24t - 0.265T)$ ; i. e., heat lost by surface radiation = heat gained from combustion—heat of combustion of gases. From this equation may be deduced the value of the use of more combustible coke (at const.  $x$ ) in that a smaller vol. of the combustion zone ( $O$ ) makes  $T$  rise until a new stationary state is reached; the heat has been compressed in a smaller vol. with higher temp. Equal effects result from higher  $t$  or smaller  $O$  (larger furnace diam.). Several more deductions can be made from this law.

B. J. C. VAN DER KOEVEN

**Heat of formation of acetalcohol.** T. P. GLADSTONE SILAW. *Can. Chem. Met.* 9, 140-1; *J. Soc. Chem. Ind.* 44, 195-6T (1925).—A simple and rather crude calorimeter is described, which was operated isothermally by running in ice water from a buret. AcH was caused to condense by adding a few drops of NaOH. The heat of condensation was 195.7 cal. per g. Variation in 9 trials  $\pm 5$  per mille.

W. P. WHITE

**The specific heats of binary mixtures.** J. W. WILLIAMS AND FARRINGTON DANIELS. *J. Am. Chem. Soc.* 47, 1490-503 (1925).—With a calorimeter already described (*C. A.* 18, 1603, 2637) the sp. heats were detd. from  $20^{\circ}$  to  $60^{\circ}$  of the following binary mixtures: benzene-toluene, chloroform- $CCl_4$ , chlorobenzene-bromobenzene, benzene- $CCl_4$ , and chloroform-acetone. All but the last may be considered as nearly ideal solns. Even in these, however, variations in the sp. heat, due in several different ways to dissociation, were found. These are critically discussed. It is evident that the changes taking place on soln. are intricate, and that dissociation phenomena are probably more important than has been recognized.

W. P. WHITE

**The heat of sublimation of carbon dioxide.** J. W. ANDREWS. *J. Am. Chem. Soc.* 47, 1597-602 (1925).—The chief exptl. difficulty was superheating, due to the excellent thermal insulation furnished by the vaporizing snow. To overcome it the snow was pressed against the flat elec. heater by a weight, and the vapor was led through more snow. Results differed 12% in 16 trials. The check on the 3rd Law by means of this result and various data of others gives a discrepancy of 5%.

W. P. WHITE

**The molecular heat of combustion of successive terms of homologous series.** P. E. VERKADE, H. HARTMAN AND J. COOPS, JR. *Proc. Acad. Sci. Amsterdam* 27, 850-66; *Verslag Akad. Wetenschappen Amsterdam* 33, 766 (1924).—Oscillations of the heat of combustion between alternate members of the dibasic acids of the oxalic series, similar to the oscillations reported and explained by Garner and Randall (*C. A.* 18, 2637) have been found, the mean increment of 156.7 cal. being affected by some variation of 3 cal., so that successive steps in the series, up to  $C_{15}$ , are 155.2 and 158.3. Some considerations are adduced, bearing on work the authors propose to do.

W. P. WHITE

**A comparison method permitting the measurement of extremely feeble currents.** B. SZILLARD. *Compt. rend.* 180, 576-8 (1925).—Feeble ionization currents as small as  $10^{-4}$  c. s. u. can be detected, and currents  $10^4$  times as strong can be measured with a precision about  $10^{-2}$  c. s. u. A regulatable current charges an electrometric segment

as the unknown current discharges it. The reading shows equality of the two

W. P. WHITE

The formation of mixed electrodes at phase boundaries. KARL HOROVITZ. *Z. physik. Chem.* 115, 424-32(1925); cf. *C. A.* 18, 193.—A theoretical discussion of the p. d. at the surface of contact of solid-liquid phases of the type, *glass-aq. soln.* The results of Gross and Halpen (*C. A.* 19, 1808) are shown to be easily derivable, but the applicability of their conclusions to the exptl. results of H. is disputed.

A. GROLLMAN

The explosive potential in carbon dioxide at high pressures. C.-B. GUYE, P. MERCIER, J.-J. WEIGLE. *Compt. rend.* 180, 1251-3(1925).—A table is given of data with the pressures, densities and the potentials obtained. There is no discussion of the data.

J. H. PERRY

Magnetic ferric oxide. RAYMOND CHEVALLIER. *Compt. rend.* 180, 1473-5 (1925); cf. Abraham and Planiol, *C. A.* 19, 2163.—Com. black, magnetic Fe oxide powder, corresponding nearly but not quite to  $\text{Fe}_2\text{O}_3$  ( $\text{Fe}_2\text{O}_3 \cdot \text{FeO}$  65:35 instead of 69:31), and contg. a trace of free Fe, on heating in air to  $350^\circ$  is rapidly oxidized to magnetic  $\text{Fe}_2\text{O}_3$ . Its magnetic properties are considerably reduced by heating at  $600-700^\circ$ , but are not completely destroyed. Heating either the black oxide or the  $\text{Fe}_2\text{O}_3$  for 15 min. at  $900^\circ$  gives a black, highly magnetic powder, which is attributed to decompn. of  $\text{Fe}_2\text{O}_3$  into  $\text{Fe}_3\text{O}_4$ .

A. PAPINEAU-COUTURE

Absorption spectra in the ultra-violet as discriminatory index between adsorption and chemical processes. A. RONCATO. *Arch. int. biol.* 74, 146-9(1924).—Ovalbumin soln. treated with reduced Fe powder shows an unaltered ultra-violet spectrum; treated with traces of an ionizable Fe salt, optical alteration follows. The first case is considered one of adsorption only, the second a chem. change. Starch-iodide shows the same ultra-violet spectrum as starch itself, indicating that there has been no chem. change.

A. T. CAMEROV

Physical properties of materials. I. Strength and related properties of metals and wood. ANON. Bur. Standards, *Circ.* 101, 204 pp.(1924).—This circular contains the values of tensile, compressive and shearing strengths; ductility; modulus of elasticity; and other related properties of pure metals and their alloys and of wood. In addition to these the properties of metals at elevated temperatures, their fatigue and impact properties, and the effect of heat treatment and cold working are given. Other properties and uses of less commonly used metals are described briefly. Graphical representation is used in many cases to show the change of the properties of a material with changing conditions.

E. J. C.

The chemical study of the wood from an old Amati violin. C. G. SCHWALBE, *Z. angew. Chem.* 38, 346-8(1925).—The sample showed 8.55%  $\text{H}_2\text{O}$ , 1.28% ash, 9.85% pentosans, methoxyl no. 20.37, alc.- $\text{C}_2\text{H}_5$  extract 2.85%, the ash being higher and the pentosans and methoxyl no. lower than for ordinary violin wood (*Picea excelsa*).

WM. B. PLUMMER

The solution of cellulose in ammoniacal copper solution (BADER) (HESS, MEX-MEX) 23.

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Sterilizing colloidal solutions. J. E. NYROP. *Danish* 34,020, Jan. 5, 1925. By means of an atomizer the liquid is sprayed into a container in which prevail a high pressure and a corresponding temp. The wall of the container or a plate mounted in it against which the liquid is sprayed is strongly cooled, and thus the liquid is cooled suddenly after first having been heated strongly by passing the hot interior of the container.

### 3—SUBATOMIC PHENOMENA AND RADIOCHEMISTRY

S. C. LIND

- A time-periodic universe and a new treatment of ether radiation. KORNEI LANCZOS. *Z. Physik* 32, 56-80(1925). F. O. A.
- Quantum magnetic tubes in rotation. H. STANLEY ALLEN. *Phil. Mag.* 49, 981-92 (1925). S. C. L.
- A space charge effect. E. W. B. GILL. *Phil. Mag.* 49, 993-1005(1925). S. C. L.
- The law of force within the atom. GEO. GREEN. *Phil. Mag.* 49, 1020-8(1925). S. C. L.
- An oscillograph study of the aluminium valve. F. H. NEWMAN. *Phil. Mag.* 49, 1029-33(1925). S. C. L.
- Low-voltage arcs in sodium and potassium vapors. F. H. NEWMAN. *Phil. Mag.* 49, 1057-64(1925); cf. *C. A.* 18, 2647. S. C. L.
- The penetrating radiation in the atmosphere. A. STÄGER. *Tech. Ind. Schweiz. Chem.-Ztg.* 1925, 59-62.—A review. N. F. HALL
- Penetrating radiation in the atmosphere at Hobart. A. L. MCAULAY AND MISS N. L. HUTCHINSON. *Papers & Proc. Roy. Soc. Tasmania* 1924, 123-5.—The leak of an insulated and guarded electrode in the center of an Fe sphere was measured. There seemed to be a diurnal variation of regular type on which were superposed large, rapid and irregular fluctuations. The causes suggested are (1)  $\gamma$ -rays from the soil. (2) a radioactive deposit on the roof. The type of variation is not fully explained. NORRIS F. HALL
- Use of scattered light in the determination of the distribution of size of particles in emulsions. A. J. STANN AND THE SVEDBERG. *J. Am. Chem. Soc.* 47, 1582-96 (1925)—The scattering of light by emulsions varies as the surface or square of the radius of the particles, indicating true reflection. In dispersed systems the ratio of the sizes of particles, having diams. 2 or 3 times the wave length of light, may be detd. directly from the ratio of the slopes of the intensity-concn. curves. Mass-distribution curves were obtained similar to those calcd. from microscopic measurements. Different alkali soaps do not shift the mass maxima although microscopic observations indicate a larger no. of small particles in going from Na to Cs soaps. By keeping the amt. of stabilizer const., an increase in  $C_{12}H_{25}$  concn. causes an exponential increase in the radius corresponding to the mass maxima. HARRY B. WEISER
- Calculation of atomic radii from the diamagnetic susceptibility. B. CABRERA. *Anales soc. españ. fis. quim.* 23, 172-80(1925).—Larmor's theory permits the calcn. of the mean radius of the electron orbits from the magnetic susceptibility without making



under the influence of the radiation. Heating discharges the color and restores the glow.  
NORRIS F. HALL

A relation between the work of removal of electrons and the electrochemical potential. A. GÜNTHER-SCHULZE. *Z. Physik* 32, 186-9(1925).—It is found that the expression  $1.3\varphi_a - E_h$ , where  $\varphi_a$  is the work of removal of an electron from a metal and  $E_h$  is the electrochem. potential, is very nearly a const. and equal to about 5.10. The variations from this value are 2.5%, Li being the only exception with a variation of 16.6%.  
H. C. U.

The motion of a free electron in a field of plane electromagnetic waves. J. FRENKEL. *Z. Physik* 32, 27-31(1925).—The equations which Halpern (*C. A.* 19, 777) had solved only approx. are integrated simply and exactly.  
F. O. A.

The mechanism in the mercury vacuum arc. A. GÜNTHER-SCHULZE. *Z. Physik* 31, 509-13(1925); cf. *C. A.* 17, 2826.—The cathode drop is close to the ionization potential. About half the current at the cathode is carried by electrons. At the anode G.-S.'s old measurements with sounding wires gave results about 4 v too high.  
F. O. A.

Electromagnetic analysis of positive rays. R. DOPEL. *Ann. Physik* 76, 1-28 (1925).—The positive rays were produced in the usual manner, the gas streaming through a fine capillary into the discharge bulb or cylinder and thence through the cathode into the inspection chamber maintained at the highest possible vacuum. The parabolas obtained by combined elec. and magnetic deflection were observed on a willemite screen, and the energy along the line obtained when the magnetic field alone was used was measured by a sensitive thermocouple. With a sufficiently high discharge potential energy curves for H show maxima on the positive side at distances approx. in the ratio  $1:\sqrt{2}:2$  and are attributed to mols., fast atoms and slow atoms. On the negative side, only fast and slow atoms are obtained, the negatively charged mols. being less stable. Addn. of O increases the relative no. of mols. In addn. to the usual features, the parabolas showed  $H_2^-$  mols. and  $He^-$  atoms. From the nature of the beading on the parabolas D. deduces the existence in the dark space of  $H_2$ ,  $O_2$ ,  $N_2$  and  $He_2$ .  
B. C. A.

The passage of cathode rays through matter. B. F. J. SCHONLAND. *Proc. Roy. Soc. (London)* 108A, 187-210(1925).—The fractions of cathode rays of velocities up to 0.55 of that of light transmitted, absorbed, and scattered back by Al, Cu, Ag, Au foils of varying thicknesses were measured more accurately (cf. *C. A.* 18, 17) under various conditions. The range of these rays was observed by 3 methods of measurement and the values at various velocities in Al are in close agreement with those calcd. on Bohr's theory of absorption (cf. *C. A.* 10, 13). Conclusion. Cathode-ray absorption is due to gradual loss of energy of the moving particles by collision with electrons in matter, where the interchange of energy takes place more freely than the usual conceptions of at. structure will allow. The absorption of cathode rays of various speeds by the atoms of a given element does not appear to show any discontinuities corresponding to those observed in X-ray absorption.  
D. S. VILLARS

Measurements on small tungsten arcs. W. DE GROOT. *Physica* 5, 121-9(1925).—Detn. of temp. (by radiation pyrometry) of the small spherical electrodes in a W arc, combined with voltage and current measurement, permits verification of some theoretical considerations on the energy balance of the electrodes. The anode receives an amt. of heat  $U_a \geq i\varphi$ ; the cathode  $U_k \leq -i\varphi + ne(V_k + fV)$ ,  $i$  is current,  $\varphi$  Richardson const.,  $n$  no. of + ions reaching the cathode,  $V_k$  ionization potential,  $f$  a factor varying from  $1/2$  to 1 and depending on the cathodic field concn. Besides the obvious condition (if  $V < 2V_k$ ) that  $ne \leq i/\varphi$ , it can be expected that  $ne < (U_k + i\varphi)/(V_k + 1/2 V)$ . In Ne these relations were completely confirmed by the results; at low current values (high potential) the fraction mentioned approaches  $1/11$ ; in A the ion current is slightly higher, also in Hg. The arc voltage, which converges to  $V_k$  at high current values in Ne and in A, approaches 15.2 V in Hg, far above  $V_k$ . J. J. Thomson's condition for an arc: voluntary electron emission of cathode  $e - ne = i_k$ , the thermionic electron stream, is satisfactorily borne out for Ne and Hg, for A the  $i_k$  values are a little too low.  
B. J. C. VAN DER HOEVEN

Radiation given out by gases through which electric discharges are passing. J. J. THOMSON. *Phil. Mag.* 49, 761-86(1925).—Previous evidence (*C. A.* 18, 2642) that ionization in the "negative glow" is due to radiation excited by cathode rays in the gas through which they pass is directly confirmed by the present expts. The radiation is too non-penetrating to pass through the glass wall of the discharge tubes, and must be detected inside the tube. The radiation can be detected by some elec. effect such as ionization produced in the gas or by a photoelec. effect. In either case the ionization of the discharge itself would interfere. Three methods were employed to sep. these

effects: (1) a very thin celluloid screen (about  $3 \times 10^{-4}$  cm. thick), which had the advantage of affording sepn. between the gas and the discharge, thus permitting variation of pressure or of the kind of gas. Even the thinnest screen transmitted less than 1% of the radiation. It was therefore necessary for the softer rays to employ (2) an electrostatic field, or (3) a magnetic field. The effect of pressure on the ionization produced in the gas was measured. The radiation consists of X-rays of far greater frequency than the characteristic radiation of the gas. The spectrum is continuous with its max. frequency corresponding to the energy of the electrons. Some of the radiation is absorbed by gases with great ease, within 2-3 cm. of air at 0.01 mm. Hg pressure. Some reflection (5%) from polished metal surfaces was observed. An expression is deduced for the energy distribution in the continuous spectrum due to the passage of electrons through a gas. S. C. LIND

A formulation of the electromagnetic laws, which permits the inclusion of the quantum theory. H. A. SENFTLICHEN. *Z. Physik* 31, 627-36 (1925). F. O. A.

The complex structure of the Röntgen-spark spectra. GREGOR WENTZEL. *Z. Physik* 31, 445-452 (1925).—W. attempts to extend the analogy between the "arc" Röntgen spectra and the spectra of the alkali metals to the case of the "spark" Röntgen spectra. Since the removal of 1 electron produces a spectrum similar to those of atoms having only 1 electron in the outer shell, the removal of 2 electrons should cause a spectrum similar to the spectra of atoms having 2 electrons in the outer shell. He predicts the type of spectra to be expected due to the removal of 2 electrons either from the same shell or from different shells. H. C. U.

The  $\beta$ -rays produced in air by short homogeneous X-rays. H. ICKE. *Compt. rend.* 180, 1257-9 (1925).—Stereoscopic photography in a Wilson cloud chamber with tungsten K radiation showed clearly 2 types of  $\beta$ -ray tracks (1) photoelectrons and (2) "fish-tracks and sphere-tracks" (Wilson). There are about 11 short tracks to 1 photoelectron as required by theory. For other results the article should be consulted. NORRIS F. HALL

The J phenomenon in X-rays. L. C. G. BARKLA. *Phil. Mag.* 49, 1033-56 (1925); cf. *C. A.* 19, 1093.—A brief general account of the J absorption discontinuities with illustrations of the results. S. C. L.

The quantum theory of scattering and dispersion. ADOLF SIEGAL. *Z. Physik* 32, 241-4 (1925). H. C. U.

The broadening of spectral lines. J. HOLTSMAKE AND B. TRUMPF. *Z. Physik* 31, 803-12 (1925).—The breadths of lines of the arc spectra of Li, Ag, Cu and Ni were measured and compared with the values calcd. from the Stark effect (*C. A.* 18, 1784). Good agreement was secured and a case of self reversal of the Ag line  $\lambda = 4055$  was explained by the peculiar splitting due to the Stark effect. H. C. U.

The relation between the completion of the electron groups of the atom and the complex structure of the spectra. W. PAULI, JR. *Z. Physik* 31, 765-83 (1925).—P. has shown (*C. A.* 19, 1658) that the usual explanation of the anomalous Zeeman effect by ascribing an angular momentum to the kernel of the atom leads to serious difficulties. In this paper he assumes that a closed shell has no angular momentum. To each electron 4 quantum nos.,  $n$ ,  $k_1$ ,  $k_2$  and  $m$ , were assigned. They are the total quantum no., the subordinate quantum no., a quantum no. which takes into account the so-called relativity doublets, and a quantum no. which measures the component of the angular momentum of the electron in the direction of a strong exterior magnetic field, resp. These have the same possible values that they have for the energy levels of the alkali metal spectra. The value of  $\Sigma m_i$  for a closed shell is 0 and therefore for a shell with one electron missing this summation has the same value as the  $m_i$  for one of the alkali-metal energy levels but with opposite sign, thus accounting for the relationship between the X-ray spectra and the optical spectra. The values of  $\Sigma m_i$  for the alkali metals, the alk. earths, the elements of the fourth group of the periodic table and for S and O are worked out in detail and the value of  $j$  (defined as the max. value of  $\Sigma m_i$ ) for the normal states is secured. The multiplicity of the normal states of Pb and S and O have been predicted. The bearing of this classification on the Stoner assignment of quantum nos. is discussed. H. C. U.

The wave length and breadth of the K-absorption limit of zinc. B. WALTER. *Z. Physik* 32, 409-14 (1925).—W. extends his previous work (*C. A.* 19, 1092). He finds that this limit must lie between the  $L_{\alpha}$  line of W and the  $L_{\gamma}$  line of Ta, i. e., between  $\lambda = 1279.17$  XU. and  $\lambda = 1281.0$  XU. The  $L_{\gamma}$  line of W is strongly absorbed by Zn while the  $L_{\alpha}$  line of Ta is weakly absorbed and thus the limit must be between these 2 lines. W. also concludes that the width of the limit is less than 2.0 XU. H. C. U.

Remarks on the intensities of the many-lined spectrum of hydrogen. G. H. DIEKE. *Z. Physik* 32, 180-5(1925).—D. points out that the Fulcher triplets are not sensitive to temp. as would be expected if these are to be regarded as 2 single branches of a rotation spectrum. He therefore maintains that each of the triplets is a rotation spectrum in itself and that the differences between the different triplets is due to vibration jumps and not as is commonly supposed to changes of the rotation quantum nos. The mol. can be excited by the absorption of radiation or by collisions with electrons, but not by collision with excited atoms if this latter assumption is made, thus accounting for the insensitivity of the lines to temp. The alternation of intensities of the triplets is similar to a similar variation found in the negative N bands. H. C. U.

The continuous spectrum of the halogens. W. STEUBING. *Z. Physik* 32, 159-62 (1925).—S. suggests that these spectra are not electron-affinity spectra but that they may be emitted by the atom because of an instability induced in the outer shell by elec. or magnetic fields. This shell of these atoms is very sensitive to the action of such fields and if they "broke" the shell a continuous spectrum might be emitted when the shell rearranged into a closed shell again. H. C. U.

The structure of the cobalt spectrum. M. A. CATALAN AND K. BECHERT. *Z. Physik* 32, 337-69(1925).—517 lines of the Co spectrum have been classified under 93 multiplets. The terms have an even-numbered multiplicity and doublet, quartet and sextet terms have been found. The normal term is a quartet  $f$ -term. All terms are "inverted." A no. of terms obey the omission principle that the azimuthal quantum no. changes by 2 or 0. The spectrum shows considerable similarity to the Fe spectrum. The magnetic moment of the normal atom should be equiv. to 6 Bohr magnetons. Tables showing the multiplets observed, their inner quantum nos., intensities and wave lengths and wave nos. are given. A comparison between the theory of the anomalous Zeeman effect and expt. is made. H. C. U.

The structure of a class of band spectra. R. MECKE. *Z. Physik* 31, 709-12 (1925).—M. points out that the intensity anomalies in band spectra always seem to appear when the emitter is a diatomic mol. having 2 like atoms. He suggests that this is related to 2 light-emitting electrons, one associated with each atom having the total angular momentum of the atom unequally divided between them. The strong lines are assumed to be emitted by the one electron and the weak lines by the jumps of the other electron. H. C. U.

The intensity of multiple lines and their Zeeman components. R. DE L. KRONIG. *Z. Physik* 31, 885-97(1925).—A permanency law is derived for the intensities of multiple lines under different conditions which agrees with the known facts. F. O. ANDEREGG

An application of the correspondence principle to the question of the polarization of fluorescent light. W. HEISENBERG. *Z. Physik* 31, 817-26(1925).—The correspondence principle may be applied to the intensity and polarization of spectral lines including fluorescent light. F. O. A.

Absorption spectra of pyrrole and its derivatives. G. V. KORSCHUN AND (MME.) K. B. ROLLA. *J. Russ. Phys.-Chem. Soc.* 55, 253-74(1924); cf. *C. A.* 19, 1420.—The displacement of bands of the spectra of pyrrole derivs. due to the introduction of Me groups has been studied on 2,5-dimethyl-, 2,3,5-trimethyl-, 1,2,5-trimethyl-, and 1,2,3,5-trimethylpyrrolecarboxylic esters; 2,5-dimethyl- and 2,3,5-trimethylamino-pyrrolecarboxylic esters; 2,3-dimethyl-, and 1,2,5-trimethylpyrrole-3,4-dicarboxylic esters; and 3,5-dimethyl-, and 2,3,5-trimethyl-1-carbamido-4-pyrrolecarboxylic esters. Also the spectrum of 1,2,5-trimethylpyrrole. Most compds. were produced immediately before examn., and either redistd. under reduced pressure or else doubly crystd. Their purity was tested either by phys. means or by analysis. When  $\text{CH}_3$  is connected to N of the pyrrole ring the bands of the absorption spectrum are shifted towards the ultra-violet. If the original pyrrole deriv. had 2 absorption bands they become combined into one, unobservable in layers thinner than those in which the absorption bands of the original derivs. have become unobservable. If  $\text{CH}_3$  occupies position 3 (from N) the absorption spectrum will be shifted towards the red end of the spectrum.  $\text{CH}_3$  in 2 and 5 positions of 1,2,5-trimethylpyrrole displace the absorption spectrum towards the red end. Three  $\text{CH}_3$  groups introduced into a mol. of pyrrole into the 1,2,5-positions cause no appreciable increase in intensiveness of absorption bands. W. M. STERNBERG

Excitation of forbidden spectral lines. P. D. FOOTE, T. TAEAMINE AND R. L. CRENAULT. *Nature* 115, 265(1925).—The Hg line  $1S - 2p_1$  (Paschen's notation), the corresponding line of Zn, and both  $1S - 2p_1$  and  $1S - 2p_2$  of Cd have been excited in the positive column of a hot-cathode discharge. The spectrum observed was of the arc type, only a few spark lines appearing. The Cd lines 2239, 2267, 2307 and 2329

A. U (belonging to the group  $2p - 2p_1$ ) were sharply absorbed by the positive glow. An unknown absorption line at 3086.7 was observed. B C A

The neon spectrum in the extreme ultra-violet. G. HERTZ. *Naturwissenschaften* 13, 489(1925)—Direct measurement of the Ne spectral lines 7357 and 7435 Å U. (difference 781 Å U) shows that they result from combination of the normal  $p$  term (inner Landé quantum no.  $J = 1/2$ ) with  $1s_2$  and  $1s_4$ ; they are the resonance lines of the unexcited Ne atom. The corresponding ionization potentials are calcd. at 21.47 and 21.57 v (21.5 measured). B. J. C. VAN DER HOEVEN

The absorption of ultra-violet light in dilute solutions. C. J. W. GRIEVESON. *Phil Mag* 49, 1006-20(1925)—An app. is sketched and a method outlined by which the relation between the concn of dil. solns and their absorption of the ultra-violet light from a spark-gap may be studied. Records are given of expts with various substances in soln in distd water, and curves are shown connecting the photoelec. effect of the transmitted light with the concn. The effect of adding certain proportions of tap-water is also investigated. It is shown that, in general, nitrates absorb more readily than some other substances, less than one part per million being sufficient to cause a measurable absorption in a depth of 10 mm of soln. Of the other Na salts examd the phosphate and carbonate absorb fairly well, the chloride and bicarbonate require much stronger solns to produce measurable effects, and the sulfate absorbs scarcely at all. Finally, the relation between absorption and thickness of soln. is examd. in a few cases. S C. L.

Emission band spectra of aromatic compounds. I. Their connection with infra-red absorption bands and a classification. J. K. MARSH. *Phil. Mag.* 49, 971-80 (1925).—The paper is largely a commentary on previous work by M. and collaborators. The spectra studied are shown to be capable of classification into (1) A benzene type characterized by bands at frequency intervals of 102 and 159 waves/mm (2) A benzene aliphatic-deriv type with band intervals of 40 or 80 in the ultra-violet. These substances under the Tesla discharge also usually give a green glow consisting of 2 bands at an interval of 160 (3) "The Blue Bands"—a spectrum produced by the Tesla discharge through a no. of substances of which BzH is an outstanding example, characterized by 3 very strong bands at intervals of 172 units (4) A condensed nuclei type, perhaps not so well established. Anthracene and derivs. show 3 or 4 characteristic bands near 4000 Å. U at intervals of 142 units, while naphthalene has a series of bands at  $1/2$  of this interval. Many substances do not give any emission, or give only one of a continuous character, and so cannot be classified. It is shown that in the infra-red bands of abs. frequency equal to the above ultra-violet frequency differences are in each case well marked and characteristic. S C. L.

The arc spectra of silver and copper. A. G. SHENSTONE. *Phil Mag* 49, 951-62 (1925); cf. C. A. 19, 606, 779—Expts. on the ultra-violet spectra of low-voltage arcs in Ag and in Cu vapor. A table of lines is given. The line absorption of Cu was found by expt. The lines in the ultra-violet are absorbed. The various combinations calcd from these data are tabulated. No series is evident in these lines. Further terms are calcd from the low-voltage arc line by using a term  $md = 51105.5$ . S C. L.

A spectroscopic study of the luminescent oxidation of phosphorus. H. J. EMELIUS AND W. E. DOWNEY. *J. Chem Soc* 125, 2491-5(1924)—It is shown that when P burns in enriched air with a flame temp. of 800°, it shows 5 bands in the ultra-violet portion of the spectrum. These occur at  $\lambda = 2190, 2475, 2530, 2630$ , and  $3275\mu$ . When P burns in air under reduced pressure with a flame temp. of 125°, it emits the same bands as above but they are resolved into narrower bands. When it glows, it emits the same narrow bands. This contradicts Petrikal's recent work, but agrees with the earlier work of Centnerszwer and Petrikal. E. P. WIGHTMAN

Excitation of spectral lines by chemical reactions. H. FRÄNZ AND H. KALLMANN. *Naturwissenschaften* 13, 441-2(1925).—Pursuing expts of Haber and Zisch, F. and K. found that on leading a mixt. of  $N_2$  gas, Na vapor and some Hg vapor into  $Cl_2$  the spectrum shows besides the Na D line the 2537 Hg resonance line, which does not appear for Hg and  $Cl$  alone; if Br is substituted for  $Cl$  the line does not appear either. This agrees with the available heat of dissociation (into atoms) of NaCl and NaBr, resp., 109,000 and 101,000 cal, and shows that in a reacting mixt. the particles do not take up more energy than corresponds to the dissociation heat. B. J. C. VAN DER HOEVEN

The testing of the law of quantum equivalence with silver halide emulsions. J. EGGERT AND W. NOODACK. *Z. Physik* 31, 922-41(1925); cf. C. A. 18, 942—In a pure emulsion each quantum of wave length  $365\mu$  decomposes one mol of AgCl. The absorption of light  $405\mu$  is 0.01 and of  $436$  is 0.003. Similar results were obtained with a Valenta emulsion. The green-sensitization with  $436\mu$  was studied and con-

cluded to be an adsorption effect resulting from photolysis. Different emulsions were studied and explanations are offered for the differences. F. O. ANDEREGG

Photochemistry of silver compounds. J. EGGERY AND W. NOODACK. *Z. Physik* 31, 942-8(1925).—The amt. of light is proportional to the sepd. Ag. AgCl is more sensitive to light of shorter wave length, cf. preceding abstr. F. O. A.

Oxalic acid-uranyl sulfate ultra-violet radiometer. WM. T. ANDERSON, JR., AND F. W. ROBINSON. *J. Am. Chem. Soc.* 47, 718-25(1925).—The photochem. decompn. of  $(\text{COOH})_2$  in  $(\text{COOH})_2 \cdot \text{UO}_2\text{SO}_4$  soln has been studied qualitatively and quantitatively in various regions of the ultra-violet spectrum. The reaction has been shown to follow zero order for a considerable extent of time; the temp coeff was 1.035 for an interval of  $10^\circ$ . E. P. WIGHTMAN

The action of light on chlorine dioxide. H. BOOTH AND E. J. BOWEN. *J. Chem. Soc.* 127, 510-3(1925).—When gaseous  $\text{ClO}_2$  is exposed to light a large quantity of red liquid forms on the walls of the vessel. The photochem. decompn., therefore, is not that usually represented in the textbooks  $2\text{ClO}_2 \rightarrow \text{Cl}_2 + 2\text{O}_2$ . The present paper is an account of expts. to det. the nature of the substances produced. On continued exposure to light, the red liquid first obtained from  $\text{ClO}_2$  becomes colorless. The reaction occurs in the absence of moisture. Mol O does not play a part, but it is shown that possibly ClO is produced. But it is not sufficient to account for the reaction. It seems clear from the work that at least one unknown Cl oxide is produced which is very active. Dry gaseous  $\text{ClO}_2$ , prepd. in darkness, and diluted with an equal vol. of  $\text{CO}_2$ , remains without decompn. over periods of several hrs. at temps. above  $85^\circ$ . Exposure for a few seconds to an elec. lamp produced a great difference in the thermal stability. Expt. showed that a little ClO added to unilluminated  $\text{ClO}_2$  exactly reproduced the thermal-decompn. curves obtained with the illuminated gas. Analysis of the residual gas showed that ClO was still present. It thus seems not unlikely that ClO is produced when light acts on  $\text{ClO}_2$ , but the explanation of this, and the formation of the heptoxide cannot be given by any simple hypothesis. E. P. WIGHTMAN

Microbalance. I. The photochemical decomposition of silver bromide. E. J. HARTUNG. *J. Chem. Soc.* 125, 2198-207(1921).—The photochem. decompn. of AgBr has been investigated by means of the microbalance. The prepn. and testing of films of very pure AgBr are described, and also an improved app. in which a sensitive film may be sealed without injury. It is shown that more than 90% of the Br may be expelled by insulating thin films of AgBr in a vacuum in the presence of suitable halogen absorbent. The rate of bromination of thin Ag films has been investigated and no evidence of the formation of Ag sub bromides has been obtained. E. P. WIGHTMAN

The photochemical decomposition of nitrosyl chloride. E. J. BOWEN AND J. F. SHARP. *J. Chem. Soc.* 127, 1020-8(1925).—B.'s and S.'s expts. on the application of the photochem. equivalence law to the photochem. decompn. of NOCl seem to throw light on the mechanism of the process, and to offer an opportunity for a criticism of the interpretation placed by Kiss (C. A. 17, 3839) on his results. Two quanta appear to be absorbed for each mol. decomposed. This makes it likely that the process is a true unimol. reaction,  $\text{NOCl} + h\nu \rightarrow \text{NO} + \text{Cl}$ , followed by spontaneous reactions reforming NOCl, such as the removal of Cl atoms giving the transitory compd. NOCl<sub>2</sub>, as suspected by Trautz and Hinck (C. A. 10, 551). E. P. WIGHTMAN

Photochemical formation of hydrogen bromide and velocity of formation of the bromine molecule from the atoms. M. BODENSTEIN AND H. LÜTKEMEYER. *Z. physik. Chem.* 114, 208-36(1924).—The velocity of combination of H and Br in moderately intense light has been investigated. The views which have been put forward to explain the phenomena of the reaction are recapitulated, and a method is described which allows a decision to be made between the various possibilities. The method consists of subjecting Br vapor and H, contained in suitable concn. in a silica vessel with plane parallel walls, to illumination from a W arc lamp. The vessel is kept at a const. temp. over the range  $160-218^\circ$ . After each illumination, the absorption of Br is measured with a spectrophotometer, from which the reaction velocity can be detd. The energy absorbed from the light is measured in the cold vessel by means of a thermopile. It is shown that the measurement of the absorbed radiation (of wave length 525, 516 and  $504\mu$ ) is not affected by temp. over the range investigated. The combination of H and Br takes place with a velocity which is about 300 times as great as that of the reaction in the dark at the same temp., and according to a law which follows from that of the dark reaction. By this, the velocity is detd. by that of the combination of H with Br atoms, existing according to the equl.  $\text{Br}_2 \rightleftharpoons 2\text{Br}$ . In light, there is in place of the velocity of spontaneous decompn., that of the decompn. of the Br mol. by absorbed light quanta. The equation for the light reaction therefore has the form  $+d[\text{HBr}]/dt =$

$k\sqrt{\text{light absorbed}} \cdot [H_2]/(1 + [HBr]/10[Br_2])$ . This is derived in all particulars from the theory of the reaction in the dark. A measurement of the absorbed light quanta allows the velocity with which Br atoms are formed and recombine to be ascertained. A comparison of the velocities in light and in the dark is supplied by associating the known dissociation equil. of Br vapor with the concn. of Br atoms. From this, the no. of collisions can be calcd., and a comparison of this with the no. of combinations to form mols. lead to the conclusion that only 1.25% of the collisions result in combination, independent of the total pressure of the gas, and of the temp. (within the narrow range investigated). This result contradicts that expected from theoretical considerations.

B. C. A.

The photolysis of dibasic acids. VOLMAR. *Comptes rend.* 180, 1172-3 (1925).—One carboxyl group of osalic acid yields  $CO_2$  under ultra-violet radiation of about 0.3 micron wave length, giving formic acid. This remaining carboxyl group requires radiation as short as 0.21 micron for its decompn. In malonic, succinic and glutaric acids both carboxyl groups decompose under approx. the latter radiation but not under the former. This is in harmony with the energy calcos. based on the law of photochem. equiv. previously proposed by V. (C. A. 18, 1612). The farther the 2 carboxyl groups are sepd., by connecting C atoms the less is their reciprocal influence; beginning with succinic acid the mutual influence has practically disappeared.

C. M. BOURON

Determination of the atomic mass of  $Li^+$  (COSTA) 2. Sensitivity of emulsions (SLATER-PRICE) 5. A comparison method permitting the measurement of extremely feeble currents (SEILLARD) 2. Activation of atoms and molecules (DHAR) 2.

BACK, E. and LANDÉ, A.: *Struktur der Materie in Einzeldarstellungen*. Vol. I. Zeemaneffekt und Multiplettstruktur der Spektrallinien. Berlin: Julius Springer, 213 pp. Unbound M. 14.40; bound M. 15.90. Reviewed in *Nature* 115, 559; *Phys. Rev.* 26, 139 (1925).

BLOCH, L.: *Ionisation et résonance des gaz et des vapeurs*. Paris: Les Presses univ. de France. 224 pp. Fr. 25.

CURIE, MAURICE: *Le radium et les radioéléments*. Preface by Mme. Pierre Curie. Paris: J.-B. Baillière & fils. 354 pp. Fr. 40, bound Fr. 50.

DAUVILLER, A.: *La technique des rayons X*. Paris: Les Presses univ. de France. 193 pp. Fr. 22.50.

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#### 4—ELECTROCHEMISTRY

COLDEN G. FINK

Electric furnace produces quality steel. C. N. DAWE. *Elec. World* 85, 1404 (1925).—By making its own valves in a Moore Lectromelt furnace an automobile concern is saving 2 c. per valve (or \$17,000 annually) over the former purchase price. The total operating cost is \$17.19 per ton, based on the production of 4 heats (av. 2230 lb. each) in 24 hr.

A. D. SPILLMAN

Modern induction furnace brass-melting practice. G. F. HUGHES and P. L. GREEN. *Brass World* 21, 205-7 (1925).—This is a discussion of brass-melting practice in the induction furnace at the Bridgeport Brass Co. The advantages of this furnace of particular note are the elimination of "spelter smoke" and the reduction of Zn losses from 1.5 to 0.5%. For continuous operation the av. life of the lining is 1,500,000 lbs. of brass, or a lining cost of about 20 c. per ton. On 24-hr. operation a 50-kw. furnace melts 12,000 lb. of 2-1 brass with 1175 kw. hr. The best efficiency is experienced with 1 man charging and pouring 2 furnaces.

A. D. SPILLMAN

The conditions of a future electric production of zinc in Norway. ØYSTEIN RAVNER. *Tids. Kemi Berge.* 5, 61-87 (1925).—The elaborate considerations are based upon much statistical material and thorough calcos. A comparison between the costs of manuf. of Zn by the muffle, electrothermic and electrolytic processes shows a decided advantage for the last two, which are nearly equal in this respect. The advantages of the electrothermic process—which is considered the one most adaptable in Norway—in comparison with the muffle process are summed up as follows: More heat economy, less skilled labor required, the CO from the furnaces may be utilized, and—perhaps most important of all—the process is suited for nearly all the usual ore species. The building

up of a Zn industry in Norway along this line is strongly recommended.

C. H. A. ROBAK

The conditions of a future electric production of zinc in Norway. BJOERN RAEDE. *Tids. Kemi Bergv.* 5, 125-45 (1925).—Like Ravner (cf. preceding abstr.) Raeder compares the 3 different methods of Zn manu. and arrives at a similar result, only he finds a decided advantage of the electrothermic process as compared with the electrolytic one.

C. H. A. ROBAK

The equilibrium of the series cryolite-alumina. G. A. ROUSH AND M. MIYAKE. *Trans. Am. Electrochem. Soc.* 48 (preprint) (1925).—The soly of  $Al_2O_3$  in cryolite in solid soln is found to extend to about 12% and of cryolite in  $Al_2O_3$  to about 77.5%. These points are confirmed by metallographic examn.

C. G. F.

Concentration and polarization at the cathode during electrolysis of solutions of copper salts. W. LASH MILLER. *J. Franklin Inst.* 199, 773-83 (1925).—In a circuit consisting of storage battery, rheostat, ammeter and cell (2 Cu electrodes in a soln. of a Cu salt) the p. d. is measured while the current is flowing. The p. d. observed is due in part to the internal-resistance drop through the cell and the remainder receives the name "polarization." The polarization is partly due to the difference in concn. at the 2 electrodes—"concn. voltage," the remainder, as long as Cu is deposited at the cathode, is the "over-voltage." The app. used is described. The exptl. work consists of: (1) measurements to check the predictions of the diffusion theory, (a) limiting current measurements, and (b) time measurements; and (2) measurements of overvoltage (the concns. given by the diffusion theory are accepted as correct and used to calc. the concn. voltages). The concns. at the electrodes during electrolysis were calcd. by the diffusion method of Weber, the equation developed by Rosebrugh and Miller being used. The periods of time to liberate  $H_2$  from acid solns. of  $CuSO_4$  or of Cu chlorides under varying current conditions agree with the predictions of the equations. By applying the concns. thus obtained, for computing the concn. voltages, the cathodic overvoltage during the electrolysis of acid solns. of  $CuSO_4$  have been detd. by the oscillograph. No "transfer resistance" is evident. Overvoltage =  $A + (B - 0.03) \log z_0/z$ , where  $z_0$  = Cu concn. in the body of the electrolyte and  $z$  = that at the cathode.  $B$  is independent of the concn. of Cu and of acid and of c. d. down to 0.1 amp./sq. dm.  $A$  is independent of Cu concn. but increases with increase in acidity.  $A$  ("instantaneous overvoltage") depends on the previous history of the electrode and has less than its normal value for a measurable time after the electrode has been anode. Several curves are shown.

W. H. BOYNTON

Periodic electrochemical phenomena. E. S. HEDGES AND J. E. MYERS. *J. Chem. Soc.* 127, 1013-26 (1925).—A review of previous work is divided: (1) where current is taken from the system, and (2) where current is led into the system. Several typical examples of periodic reactions have been investigated from the electrochem. standpoint, by means of an app. in which the elec. and chem. effects of the reactions were registered simultaneously. With activated metallic couples dissolving in HCl or  $NH_4Cl$ , the p. d. between the couple as a whole and the soln., and between the 2 components of the couple undergo periodic fluctuations which synchronize with the periodic evolution of gas. A p. d. exists between the activated and inactive forms of the metal. Some new reactions involving the periodic deposition of metals are described. The change consists in an alternate formation and dissolution of a metallic film, which is accompanied by a corresponding oscillation of the electropotential. In some cases the rate of evolution of  $H_2$  is also periodic. Examples are given of "auto-periodic" reactions where one electrode serves as the receiving metal and as the activating agent. Numerous curves are shown.

W. H. BOYNTON

Electrolysis of water. The Knowles electrolytic cells for the production of chemically pure hydrogen and oxygen. H. SARROY DU BELLAY. *Rev. prod. chim.* 28, 289-93, 325-9 (1925).—Description of the cell, its operation and merits, and of some installations actually in operation.

A. PAPINEAU-COUTURE

The production of stibine at an antimony cathode in alkaline solution. II. The variation of the percentage yield of stibine with the temperature of the electrolyte and with the hydrogen concentration (activity) in the electrolyte. E. J. WEEKS. *Rec. trav. chim.* 44, 201-5 (1925); cf. *C. A.* 19, 443.—Examn. of the tables given in the previous paper shows that the yield of  $SbH_3$  depends on the temp. In the present paper the temp. equation is deduced. If  $\gamma$  = % yield,  $T$  = the abs. temp.,  $H$  = H concn. in the electrode,  $C$ ,  $C_1$  and  $C_2$  = consts., then  $\gamma + 20 = C/T$ ,  $T = C_1 - C_2 \log H$ .

E. J. W.

An electrochemical method for estimating the corrosion of iron and steel. H. BEENY. *Trans. Am. Electrochem. Soc.* 48 (preprint) (1925).—Tests were undertaken to determine the influence of Mn and the corrosion of a large no. of hypo-eutectoid steel

samples. The electrolytic method proposed by Desch and Whyte, using a 5% NaCl soln. and a Pt cathode, was first tried but results were not satisfactory, largely because of a rapid polarization of the Pt electrode. Accordingly, a new app. was devised using a Au cathode, with an immersed surface 40 times that of the polished steel specimen which was made anode. Cathode polarization was thus minimized. The electrolyte was 0.2% NaCl soln. The progress of corrosion was observed through the microscope. The quantity of electricity liberated by the corrosive reaction itself was measured electrically and also analytically. The 2 values check indicating "beyond all doubt that the corrosion has been entirely electrochemical." The whole of the Fe corroded entered soln. in the ionic condition. Expts. were then made to det. the effect of varying the quantity of air ( $O_2$ ) in soln. upon the rate of corrosion. Results indicate that the "purely chemical" effect either does not exist at all or is extremely slow and unimportant compared with the electrochem. corrosion reaction. A further improvement in the app. was made by rapidly rotating the Au cathode and thus reducing the effect of cathode polarization by H still further. Mn sulfide appears to stimulate local corrosion. Mn as carbide, and in solid soln., has little or no action upon the corrodibility of the metal. Photomicrographs of the corroded areas are shown and discussed. Atm. corrosion is fundamentally electrochem. C. G. F.

Studies in electroplating. V. Agitation. W. E. HUGHES, *Metal Ind.* (London) 26, 257-60, 457-8, 479-81, 506-8(1925).—H. points out the advantages of agitation, its mode of action and its effect on the structure of electrodeposits. Agitation is sometimes disadvantageous where finishing after plating is undesirable, and where the cost of mech. agitation is unwarranted. Natural and artificial means of agitation are classified. Particular emphasis is laid upon mech. methods for moving the cathode, the anode or the electrolyte. The advantages and disadvantages of each method for different purposes are given. W. H. BOYNTON

Effect of nitrates on current efficiency of plating solutions. P. A. NICHOL AND O. P. WATTS. *Trans. Am. Electrochem. Soc.* 48 (preprint)(1925).—Upon the addn. of 40 g. per l. of  $NaNO_3$  to a  $NiSO_4$  plating bath no Ni deposit was obtained. Solns. of the nitrates of Zn, Cd, Co, Ni and Fe were tried, but no satisfactory results obtained. On the other hand Pb and Cu nitrate baths gave cathode efficiencies of 97% and 99%, resp. An appreciable drop in current efficiency was obtained upon the addn. of  $NaNO_3$  to  $AgCN$  baths. In general, nitrates are to be avoided in plating baths. C. G. F.

Valve impedance. W. H. DATE. *Electrician* 94, 688(1925).—If impedance alone is required, rapid measurement may be made by use of the usual high-tension and low-tension battery supply, a milliammeter or galvanometer, a double-throw switch and a resistance-box reading up to 5000 ohms. A diagram of connections is shown. Readings, once the app. is set up, are taken in a few seconds and a simple tabulation permits rapid calcn. of the impedance for various values of the high-tension battery and of the grid voltage (dry cells) at which the impedance of the valve is desired. The method is useful to show the variation in impedance over the range of a characteristic curve. W. H. BOYNTON

#### Electrodeposition of rubber (SHEPPARD, EBERLIN) 30.

AUDUBERT, RENÉ: *Cours d'Électrochimie. Notions théoriques et applications de l'électrochimie.* Preface by Paul Jauet. Paris: Librairie de L'Enseignement Technique. 3 Rue Thenard. \$3 00.

LE BLANC, MAX: *Lehrbuch der Elektrochemie.* 11th and 12th ed. revised. Leipzig: Oskar Leiner. 419 pp. 11 M., bound 13 M.

### 5—PHOTOGRAPHY

C. E. K. MEES

Studies in photographic sensitivity. VI. The formation of the latent image. S. E. SHEPPARD, A. P. H. TRIVELLI AND R. P. LOVELAND. *Sci. Ind. Phot.* 5, 29-33; *J. Frank Inst.* 200, 51-83(1925); cf. C. A. 19, 614.—Svedberg's hypothesis, that all of the "specks" of photosensitizing substance in the grains of an emulsion are equally sensitive, cannot be true. The same exptl. results invalidate a premise of Silberstein's theory. These specks of foreign material cannot be photosensitive as suggested by Toy if the photochem. equivalence principle holds since they do not affect the optical sensitivity of the AgBr. It is suggested that the sole function of the specks is to collect

about them the Ag atoms produced by the photochem. decompn. of AgBr. There is no catalysis of photochem. decompn. but only an (auto) catalyzed orientation of the decompn. The action of light itself can supply centers in the absence of foreign material. Thus the conditions of both Svedberg's and Silberstein's theories hold for the higher exposures and larger grains. The theory suggested explains the influence of grain size on apparent photosensitivity.

C. E. K. MEES

Some modern views on the sensitivity of emulsions. T. SLATER-PRICE. *Phot. J.* 65, 298-311(1925).—Since many substances emit electrons when illuminated, the first action of light on Ag halide may be the detachment of an electron. The decay of the latent image would be due to the electron's return. Electronic interchange is greatly modified by the presence of ions adsorbed on the surface of the grains spoiling the symmetry of the space lattice. Adsorbed Ag, halogen and hydroxyl ions are especially active. Grains may be sensitized by the presence of colloidal Ag, a print-out emulsion which has been slightly exposed to violet light may be blackened completely in red because of the Ag first liberated sensitizing to the longer wave length. The sensitive centers in high-speed emulsion grains may be more apparent than real. They may be merely the accidental places where the Ag first deposits, or they may more probably represent pre-existing deposition centers, or even activity centers. The action of light on the grain does not obey the Einstein photo-equivalence laws except perhaps under sp. conditions.

K. C. D. HICKMAN

New desensitizing dyes. B. HOMOLKA. *Phot. Ind.* 1925, 347.—When a chromophore group, especially an amino group, is introduced into the phenanthrene nucleus of flavindulines, green basic dyes result which have powerful photographic desensitizing properties. The simplest representation of this group of dyes can be made by heating equimol. quantities of  $\alpha$ -aminodiphenylamine and 2-aminophenanthrenequinone in the presence of HCl in alc. soln. The resulting violet cryst. compd.,  $C_{25}H_{11}N_3Cl + H_2O$ , is easily sol. in alc. and  $H_2O$ , with a green color, is a powerful desensitizer and does not stain gelatin. Substances of similar properties can be obtained by substituting for the  $\alpha$ -aminodiphenylamine its homologs.

M. L. DUNPON

Solarization, and photographic reversal by desensitizers. B. H. CARROLL. *J. Phys. Chem.* 29, 693-704(1925).—The spectral sensitivity of ordinary plates for solarization is the same as that for the normal latent image; specific reversing action by the red and infra-red (Herschel effect) is non-existent for AgBr-gelatin. Reversal by a second exposure on pre-exposed plates bathed with desensitizers is most rapid with fine-grained plates; the spectral sensitivity is detd. by the absorption spectrum of the desensitizer and does not extend past  $1\mu$  in any case studied (cf. C. A. 18, 2473). All types of desensitizers are capable of destroying latent image in the dark, although the velocity differs greatly.

B. H. CARROLL

Standard development. W. CLARK. *Phot. J.* 65, 76-89(1925).—Methods of obtaining uniform development, the effects on the characteristic curves of a plate of varying developer compn., effects of temp. variation, and the compn. of the standard developer are discussed. Exptl. work and data are given to show the results obtained in varying each factor which enters into development. Practical recommendations are given for securing a max. uniformity of development of sensitometric strips.

M. A. YERGER

New contribution to simultaneous development and fixation. A. AND L. LUNIERE AND A. SEYEWETZ. *Bull. soc. franc. phot.* 12, 9-11(1925).—Two formulas for a combined developing and fixing bath were tested and found to produce too much dichroic fog and to require too much exposure. One contained metaquinone and the other diamino-phenol. The following formula was found superior:  $H_2O$  100 cc.,  $Na_2SO_3$  (anhyd.) 40 g., diamino-phenol-HCl 0.5 g.,  $Na_3PO_4$  2.0 g.,  $Na_2SiO_3$  (cryst.) 2.5 g.

C. H. I.

The development of a silver bromide negative with ammonia. A. P. H. TRIVELLI AND S. E. SHEPPARD. *Kolloid-Z.* 36, 236(1925); cf. C. A. 7, 1448, 15, 3254; 18, 503; 19, 216.—This is a continuation of the discussion of Lüppo-Cramer's "Zerstaubungstheorie" which T. and S. think neither necessary nor appropriate for the explanation of development by  $NH_3$ . Microscopic observation shows no such breaking up of crystn. centers as the theory of L.-C. demands.

F. E. BROWN

Function of gelatin in development. T. S. PRICE. *Phot. J.* 65, 94-5(1925).—Pure AgBr, though unexposed to light, is reduced by a photographic developer. Gelatin has a retarding influence on this reduction, making the gelatin emulsion possible. P. discusses the mechanism of this action.

R. S. SCOTT

Fog due to a metal hydroquinone developer. L. T. BRANCH. *New Phot.* 5, 306-7(1925).—B. believes that developer fog is frequently caused by an unsuitable ratio between the carbonate and sulfite content. For best results with a negative developer the ratio of carbonate to sulfite should be about 1:4 and there should be about  $1/2$  as

much elon present as hydroquinone. For bromide and gas light papers, the carbonate to sulfite ratio should be between 2:1 and 1:1 while the metol and hydroquinone should be in the ratio of 1.4 approx. J. I. CRABTREE

Use of potassium metabisulfite in developers. P. STRAUSS. *Phot. Ind.* 1925, 317-8— $K_2S_2O_5$  is advantageous for use in a 2 soln developer, as it preserves the developing agent from oxidation. Most developing agents are sol. in  $K_2S_2O_8$  soln; exceptions are neol, glycine and eikonogen. On neutralizing with carbonate, some bicarbonate is formed which acts like bromide to diminish fog. 222 g of  $Na_2S_2O_3$  corresponds to 504 g of  $Na_2SO_3$ . More alkali is required to neutralize the  $Na_2SO_3$ , and no advantage in cost is shown. M. L. DUNDON

"Hypo" elimination. A. E. AMOR. *Brit. J. Phot.* 72, 18-9(1925)—Prints fixed in a 20% "hypo" soln were washed by changes of  $H_2O$ , or eliminator soln, for 2 min. with agitation. The "hypo" content was estd. by the starch iodide method. A 0.2% NaOH soln and  $K_2S_2O_8$  soln. were found to be the 2 most efficient eliminators, but neither soln. was considered an improvement over careful washing in running  $H_2O$ . G. E. MATTHEWS

Report of the conference on the standardization of plate-testing methods. *Phot. J.* 65, 290-2(1925)—A low temp source, preferably the Eastman acetylene burner of 15-20 c. p., is advocated to give an illumination between 4 and 20 candle meters on the plate surface in conjunction with a non-intermittent exposure and a time scale. Dish development is recommended by the brush method of Clark in an H & D pyro soln. of  $1/4$  strength, without preliminary soaking, followed by an acid stop bath, plain fixation and drying in alc. Densities should be measured on photometers calibrated from standard testing lab. wedges and the results expressed in the form of characteristic curves for 3 times of development, the underexposure portion being rendered separately. K. C. D. HICKMAN

Standardization of plate-testing methods. F. F. RENWICK. *Phot. J.* 65, 57-9 (1925).—A general scheme of testing should combine convenience in use with efficient latitude in procedure to do justice to differing emulsions. The light source should not be screened and should be a conventional primary standard reserved for the calibration of a W filament lamp with which the actual tests should be made. The limits of intensity and exposure should be arranged to suit the material. K. C. D. HICKMAN

Effect of wave length on the characteristic curve of a photographic plate. T. THORNE-BAKER. *Phot. J.* 65, 60-2(1925)—For const time of development,  $\gamma$  increases considerably with the increase in wave length of the exposure light.  $\gamma$ -Infinity, however, is practically const over the range 0.17-700  $\mu$ . If development is carried out to infinity the color of the light source will be without influence on the result. M. A. Y.

Law of the blackening of the photographic plate at low densities. E. A. BAKER. *Proc. Roy Soc Edinburgh* 45, Pt 2, 166-86(1925)—B uses the expression  $\log_e I/I_0 = a\Delta + bT + 1/2(c\Delta^2 + d\Delta T + 1/2(eT^2)) +$ , where  $\Delta = f$  (density), and  $T = f$  (time). This is reduced by a method developed by R. A. Sampson, *Monthly Notices Roy Astron Soc* 85, 212(1925), introducing 2 other consts  $p$  and  $q$ , where  $p$  is Schwarzschild's exponent, and  $q$  may be defined by  $p/q = \gamma$ . B finds for specular densities less than unity that  $p$  and  $q$  are relatively const. over a range of exposure times of 1-100,  $p$  decreasing slightly with increasing exposure time. The coeff "b" in the original expression varies with different emulsions of the same plate; "d" is practically negligible for low densities, and "e" depends on the wave length of the exposing light. An extensive bibliography on the reciprocity law is appended. V. C. HALL

Cause and removal of bronzing in the printing-out process. F. FORMSTRECHER. *Phot. Ind.* 1925, 347-8—All good printing-out papers rich in Ag show bronzing in the heavy densities if overprinted. This is caused by the formation of Ag in a coarse, cryst, metallic appearing form. If not too great, it disappears during toning and fixing. In case of serious bronzing special treatments are suggested. M. L. DUNDON

Daylight filter for photographic purposes. H. NAUMANN. *Phot. J.* 65, 59-60 (1925)—The following formula is given for prep of a W to daylight filter: toluidine blue, 1.20 g; filter violet, 0.10 g., last red D, 0.10 g., methylene blue, 0.20 g., rapid filter red 1, 0.16 g., and orange, 11.008 g per sq m. These dyes are dissolved separately and the soln is mixed. After the gelatin is added, the mixt. is applied. M. A. Y.

## 6—INORGANIC CHEMISTRY

A. R. MIDDLETON

Purification of potassium cyanide and sodium cyanide. Their melting points. GRANDADAM. *Compt. rend.* 180, 1598-9(1925).—KCN and NaCN were purified by crystn. from liquid  $\text{NH}_3$ . The soly. of each of these salts in liquid  $\text{NH}_3$  at  $33.5^\circ$  is about 4 parts per 100. The m. ps. of the two pure salts were detd. in a Ag crucible in an atm. of dry N. Temps. were measured with a Ag-Au thermocouple. NaCN m.  $563.7 \pm 0.3^\circ$ ; KCN m.  $634.5 \pm 1^\circ$ .

R. L. DODGE

Some xanthates. B. CECCHIETTI. *Gazz. chim. ital.* 55, 104-5(1925).—Vitali in studying  $\text{CS}_2$  qualitatively observed that when  $\text{CS}_2$  is shaken up with  $\text{H}_2\text{O}$  and then treated with a few drops of  $\text{EtOH}$  and  $\text{KOH}$  soln. and finally  $(\text{NH}_4)_2\text{MoO}_4$  and dil.  $\text{H}_2\text{SO}_4$  with cooling a wine-red color is formed which he attributed to the formation of Mo xanthate. C. has repeated this test on a larger scale and sepd. as a ppt. Mo xanthate,

$\text{Mo} \begin{pmatrix} \text{S} \\ \diagup \\ \text{C} \text{OEt} \\ \diagdown \\ \text{S} \end{pmatrix}_2$ , a black powder, m.  $108^\circ$  (decompn), insol in most solvents, sol. in  $\text{CS}_2$  and  $\text{CCl}_4$ . The same mixt treated with  $\text{CdSO}_4 + \text{dil. H}_2\text{SO}_4$  sepd. Cd xanthate,  $\text{C}_4\text{H}_{10}\text{O}_2\text{S}_2\text{Cd}$ , yellow, it becomes red at  $159^\circ$ ; decomps without melting at  $270^\circ$ .

E. J. W.

The reactivity of complexly bound organic compounds. HANS REIHLEN, RICHARD JULIG AND RUDOLF WITTIG. *Ber.* 58B, 12-9(1925).—This is an investigation of the way in which the reactivity of certain org. groupings is influenced by their having entered into the formation of complex compds. Chromi-acetylacetonate reacts with the calcd. or an excess amt. of Br in alc. soln. to form tri- $\gamma$ -bromoacetylacetonato-chromium,  $\text{H}_3\text{C} \cdot \text{C}=\text{CBr}=\text{C} \cdot \text{CH}_3$ . This compd. is insol. in  $\text{H}_2\text{O}$  and alc., but sol. in  $\text{CHCl}_3$ ,



from which it crystallizes in red-violet crystals. If the reaction takes place in  $\text{CHCl}_3$  soln. 6 atoms of Br are added, HBr is evolved, and there is formed tri- $\alpha, \gamma$ -dibromoacetylacetonato-chromium as deep red pseudo-octahedra,  $\text{H}_3\text{C} \cdot \text{C}=\text{CBr}=\text{C} \cdot \text{CBrH}_3$ . It



is stable in boiling alc.,  $\text{HCl}$  and  $\text{NaOH}$ ; insol. in alc. and  $\text{H}_2\text{O}$ , slightly sol. in ether and  $\text{AcOH}$ , and more so in  $\text{CHCl}_3$ . The soln. in ether and in  $\text{AcOH}$  is green but gives red crystals, and very small crystals appear green. The first reaction involves the normal addition of Br at the double bond in the complex followed by the splitting off of  $1/2$  the Br as HBr. The second reaction involves (1) the same reaction, (2) a shifting of the double bond and the addition of Br to it, and (3) the splitting off of HBr and the return of the double bond to its original position. Hence the fact that a double bond belongs to an inner-complex ring system does not affect adversely its additive or shifting powers. A second series of reactions shows that substitution can be made in the nucleus of the phenyl radical of complexly bound pyrocatechol. E.g.,  $\text{CHCl}_3$  reacts with the Na or K salt of dipyrocatechol-diaquo-nickeloate giving protocatechualdehyde. For short reaction times the yield is less than with free pyrocatechol, but for longer reaction times it is greater. With the K salt of tripyrocatechol-chromiate,  $\text{CHCl}_3$  gives only 60% normal yield of protocatechualdehyde. This is a true inner-complex salt and the pyrocatechol is more firmly bound than in the less complex Ni salt. R. H. I.

Double chromates of the rare earths and alkali metals. I. Double chromates of lanthanum and potassium. G. CARONNI. *Atti accad. Lincei* [v] 33, ii, 416-20 (1924).—Investigation of the isotherm for  $25^\circ$  of the system  $\text{La}_2(\text{CrO}_4)_3\text{-K}_2\text{CrO}_4\text{-H}_2\text{O}$  indicates the existence of hydrated double chromates with the components in the mol. proportions 1:1:2, 1:3:2, 1:4:2, 1:4:5:2, and 1:5:2.

B. C. A.

Double sulfates of rare earth and alkali metals. II. Neodymium and potassium sulfates. F. ZAMBONINI AND V. CAGLIOTI. *Atti accad. Lincei* [v] 33, ii, 385-9 (1924).—The various double neodymium K sulfates are described. Cf. C. A. 19, 2309.

B. C. A.

A nitroprusside of bivalent iron. A. UNGARELLI. *Gazz. chim. ital.* 55, 118-27 (1925).—Many metallic compds. contg. the NO group are known, but in only a few is anything precise known concerning the function of the NO group in the mol. The various types of compds of this sort are reviewed. The constitution of the nitroprussides has not been fully clarified (Hofmann, *Ann.* 312, 1(1900); Miolati, *Rev. gen. chim.* 3, 197(1900)) and direct demonstration that Fe may not be quadrivalent and that

these compds do not contain a hyponitrous acid residue is lacking. U. has attempted

to prep. Na hyponitriteferropentacyanide (I)  $\left[ \text{Fe} \begin{smallmatrix} \text{NO} \\ (\text{CN})_5 \end{smallmatrix} \right] \text{Na}_4$ , by treating Na aquocyanide (II)  $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]\text{Na}_4 \cdot \text{H}_2\text{O}$  with Na hyponitrite. Twenty g. com Na nitroprusside + 20 g.  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$  in 80 cc  $\text{H}_2\text{O}$  were treated with 7 g.  $\text{NH}_2\text{OH} \cdot \text{HCl}$  in  $\text{H}_2\text{O}$  in small portions with ice-cooling. After an hr. 300 cc. EtOH were added and II was pptd. as a black tar. This was redissolved in  $\text{H}_2\text{O}$  and repptd. with EtOH several times. Each time some II was obtained as a yellow cryst powder. Five g. of this powder in 80 cc.  $\text{H}_2\text{O}$  were treated with 2 g.  $\text{Na}_2\text{N}_2\text{O}_4 \cdot 5\text{H}_2\text{O}$  (Divers, *J. Chem. Soc.* 75, 96(1899)) by reduction of  $\text{NaNO}_2$  with Na Hg. The yellow soln. of II becomes green and on adding MeOH I,  $[\text{Fe}(\text{CN})_5\text{NO}]\text{Na}_4 \cdot 9\text{H}_2\text{O}$ , seps as a silky yellow ppt. The anhyd. salt is hygroscopic. In  $\text{H}_2\text{O}$  soln. this salt has the simplest possible mol as shown by the mol wt. detns and therefore contains but half of a  $\text{H}_2\text{N}_2\text{O}_4$  mol. Solns. of I give the reactions characteristic of all ferropentacyanides with  $\text{Fe}^{++}$ ,  $\text{Fe}^{+++}$ , Cu, Co, Ni, Ag, etc., salts. The characteristic nitroprusside reaction of  $\text{Na}_2\text{S}$  does not occur with I. Attempts to obtain  $[\text{Fe}(\text{CN})_5(\text{NO})]\text{Na}_3$  by oxidation of I failed. E. J. W.

Addition products of selenium dioxide with the halogen acids. C. W. MUEHLBERGER AND V. LENHER. *J. Am. Chem. Soc.* 47, 1842-4(1925).—The compds  $\text{SeO}_2 \cdot 2\text{HCl}$  and  $\text{SeO}_2 \cdot 2\text{HBr}$  (Ditte, *Ann chim phys* [5] 10, 82(1877)) are shown to be identical with the hydrates  $\text{SeOCl}_2 \cdot \text{H}_2\text{O}$  and  $\text{SeOBr}_2 \cdot \text{H}_2\text{O}$  both in physical properties and in chem reactions. A new method is given by which  $\text{SeOCl}_2$  can be produced from  $\text{SeO}_2 \cdot 2\text{HCl}$ , four parts being treated with one part of  $\text{H}_2\text{SO}_4$  (d 1.84). Sepn. is most complete when the final concn. of  $\text{H}_2\text{SO}_4$  becomes about 70%. Ditte's  $\text{SeO}_2 \cdot 4\text{HBr}$  was confirmed but no evidence obtained for his  $\text{SeO}_2 \cdot 5\text{HBr}$ .  $\text{SeO}_2 \cdot 2\text{HBr}$ , which he believed not to exist, was obtained. It can be dehydrated by  $\text{SeO}_2$ . A. R. M.

Azido-carbon disulfide. II. Reaction of azido-carbon disulfide and of free thiocyanogen with hydronitric acid in certain non-aqueous solvents. F. WILCOXON, A. E. MCKINNEY AND A. W. BROWNE. *J. Am. Chem. Soc.* 47, 1917-21(1925), cf. C. A. 18, 27.—The reactions were studied in  $\text{Et}_2\text{O}$  solns. They were found to be  $(\text{SCSN})_2 + 8\text{HN}_3 = 2\text{NH}_4\text{SCN} + 2\text{S} + 13\text{N}_2$  and  $(\text{SCN})_2 + 8\text{HN}_3 = 2\text{NH}_4\text{SCN} + 11\text{N}_2$ . Evidence was obtained that the former takes place in 3 principal stages: (a)  $(\text{SCSN})_2 = 2\text{N}_2 + 2\text{S} + (\text{SCN})_2$ ; (b)  $(\text{SCN})_2 + 2\text{HN}_3 = 2\text{HSCN} + 3\text{N}_2$ ; (c)  $\text{HSCN} + 3\text{HN}_3 = \text{NH}_4\text{SCN} + 4\text{N}_2$ .  $(\text{SCSN})_2$  is thus indicated as a convenient source of free  $(\text{SCN})_2$ . A. R. M.

The group of volatile hydrides. FRITZ PANETH AND E. RABINOWITSCH. *Ber.* 58B, 1138-63(1925).—The prepn of pure  $\text{GeH}_4$  is described. 1.5 g  $\text{GeO}_2$  was dissolved in 40 cc concd.  $\text{H}_2\text{SO}_4$ , dild. to 200 cc and, in the app. used for  $\text{SnH}_4$  (C. A. 19, 1228), electrolyzed between Pb electrodes with 15 amp. current strength and intensive cooling with ice. The  $\text{H}_2\text{-GeH}_4$  was washed with alk.  $\text{Pb}(\text{AcO})_2$ ,  $\text{GeH}_4$  condensed by liquid air and fractionated in a Stock vacuum app. Vapor pressures were detd. at  $-147^\circ$  to  $-87^\circ$ , B p.,  $-88.5^\circ$ ; m p.,  $-164.5^\circ$ . All known thermic data for the volatile hydrides are assembled and treated as functions of the period number. The resulting sets of curves parallel rather closely the corresponding curve for the rare gases. The hydrides of Group IV are next above the rare gases in volatility, then follow the RH and  $\text{RH}_2$  hydrides; the  $\text{RH}_2$  hydrides form the least volatile group. Extrapolation of the curves gives for the still undetd. b. p. of  $\text{PbH}_4$ ,  $-13^\circ$ , of  $\text{BiH}_3$ ,  $+22^\circ$ ; of  $\text{PoH}_2$ ,  $+37^\circ$ . The curves indicate that in many cases the data are in error and require redetn. The m p. of radon is indicated as about  $160^\circ$  abs instead of  $202^\circ$  abs. Gray and Ramsay (C. A. 3, 2903) noticed a sharp change in fluorescence color at  $155^\circ$  abs. The melting and boiling pts. of the hydrides and hafides of Si, Ge and Sn when plotted against the period numbers of the halogens ( $\text{H}_2 = 1$ ,  $\text{Cl}_2 = 3$ ,  $\text{Br}_2 = 4$ ,  $\text{I}_2 = 5$ ) form similar curves and closely parallel the corresponding curves of the halogens. A. R. M.

Higher oxides of silver. I.  $\text{Ag}_2\text{O}_3$ . F. JIRSA. *Chem. Listy* 19, 3-9(1925).—Higher oxides of Ag are formed by the energetic oxidation of metallic Ag or of Ag salts, and contain either the monoxide,  $\text{Ag}_2\text{O}$ , alone or the sesquioxide,  $\text{Ag}_2\text{O}_3$ , together with the monoxide and varying amts. of the Ag salt from which they are prepd. The higher oxide does not appear to be capable of sep. existence and is easily decomposed by heating the compds, contg. it to temps. just below  $100^\circ$ ; e. g.,  $\text{Ag}_2\text{NO}_3 = 3\text{Ag}_2\text{O}_3 + \text{AgNO}_3 + \text{O}_2$ . By extg. the product of this reaction with boiling water the oxide,  $\text{Ag}_2\text{O}_3$ , remains insol in an almost pure state. This oxide catalytically accelerates the decompn. of the sesquioxide. B. C. A.

The action of certain reagents upon ozone. L. I. SMITH. *J. Am. Chem. Soc.* 47, 1850-3(1925).—The effect upon the decompn. of ozone of  $\text{H}_2\text{O}$ , concd  $\text{H}_2\text{SO}_4$ , 5%

$\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{O}$  followed by concd  $\text{H}_2\text{SO}_4$ , acidified  $\text{KMnO}_4$  soln.,  $\text{P}_2\text{O}_5$  that had been resublimed in a current of  $\text{O}_2$  is negligible. When passed through 5%  $\text{NaOH}$  soln., however, the ozone in a 6% ozone- $\text{O}$  mixt. was practically completely destroyed even when the gas flow was as high as 531 per hr. Commercial  $\text{P}_2\text{O}_5$  decomposes ozone rather quickly; with a gas flow of 28 l. per hr. the ozone content of an ozone- $\text{O}$  mixt. was reduced from 8.65% to 1.48% by passage through 2 U-tubes filled with  $\text{P}_2\text{O}_5$  and glass wool. The active agent in the commercial  $\text{P}_2\text{O}_5$  was not detd., but was found to be removed by resubliming in  $\text{O}_2$ . R. L. DODGE

The reaction of arsenious anhydride on alkaline carbonates. B. L. VANZETTI. *Gazz. chim. ital.* 55, 110-8 (1925).—The conflicting and incomplete data on the action of  $\text{As}_2\text{O}_3$  with sol carbonates are fully reviewed.  $\text{As}_2\text{O}_3$  was treated with alk. carbonate so that the  $\text{CO}_2$  evolved could be collected. It was found that even on heating  $\text{CO}_2$  is eliminated slowly and incompletely. The reaction was studied quantitatively in an app in which a stream of  $\text{CO}_2$ -free  $\text{H}_2$  could be passed to expel the  $\text{CO}_2$  from the reaction soln. The  $\text{CO}_2$  was collected in  $\text{KOH}$  soln with the usual precautions. The  $\text{CO}_2$  evolved corresponds to the equation:  $3\text{Na}_2\text{CO}_3 + \text{As}_2\text{O}_3 \rightarrow 2\text{Na}_3\text{AsO}_3 + 3\text{CO}_2$ . The reaction can be made to go to completion only by removing the  $\text{CO}_2$ . All carbonates can doubtlessly be decompd. in this way giving presumably  $\text{M}_2\text{AsO}_3$  but these need not necessarily be recovered from the soln but are largely hydrolyzed. E. J. W.

The existence of alkaline orthoarsenites. B. L. VANZETTI. *Gazz. chim. ital.* 55, 106-10 (1925).—The literature concerning the uncertain existence of alkali orthoarsenites is reviewed. V attempted to prep. the unknown  $\text{Na}_3\text{AsO}_3$  by the reaction  $\text{As}_2\text{O}_3 + 6\text{NaOH} \rightarrow 2\text{Na}_3\text{AsO}_3 + 3\text{H}_2\text{O}$ . Solns of known amts of Na in abs  $\text{MeOH}$  and  $\text{EtOH}$  were prepd.  $\text{As}_2\text{O}_3$  in the ratio of 1 mol to 6 atoms of Na was added. The  $\text{As}_2\text{O}_3$  was easily dissolved in  $\text{MeONa}$  soln but not in  $\text{EtONa}$  soln. even after long boiling. The excess  $\text{MeOH}$  was distd off on the  $\text{H}_2\text{O}$ -bath. The remaining soln. on evap. in a vacuum desiccator sep'd a white crust. The 1st fractions were nearly 80%  $\text{Na}_3\text{AsO}_3$ ; the last fractions contained 20%. The solns. with  $\text{AgNO}_3$  pptd yellow  $\text{Ag}_3\text{AsO}_3$ . Attempts to isolate  $\text{Me}_3\text{O}$  in liquid form (it b.  $-23^\circ$ ) failed but an easily combustible gas having the odor of  $\text{Me}_2\text{O}$  was obtained. The reaction between  $\text{MeONa}$  and  $\text{As}_2\text{O}_3$  is not complete even on prolonged boiling. With  $\text{K}_3\text{AsO}_3$  the sirup could not be crystd. This reaction is not a good method for obtaining pure alkali orthoarsenites. E. J. WITZEMANN

COPAUX, H. and PERPÉROY, H: *Chimie minérale. Description des éléments chimiques et de leurs propriétés.* Paris: A. Colin. 3 Vols. Each vol. Fr. 6, bound Fr. 7.

Textbook of Inorganic Chemistry. Edited by J. Newton Friend. Vol. III. Pt. 1. The Alkaline Earth Metals by M. S. Burr. London: Charles Griffin & Co., Ltd. 346 pp. 20s. net. Reviewed in *Chem. Trade J.* 77, 10 (1925). Cf. C. A. 18, 2481.

## 7—ANALYTICAL CHEMISTRY

WILLIAM T. HALL

Application of indicators. T. KAKU. *J. Pharm. Soc. Japan*, No. 518, 63-71 (1925).—Using  $\alpha$ -dinitrophenol, methyl orange, Congo red, methyl red, hematoxylin,  $p$ -nitrophenol,  $m$ -nitrophenol, neutral red, phenolphthalein, and thymolphthalein, K. titrated a strong acid with a strong base, a weak acid with strong base; strong base with weak acid, a weak base with a strong acid; a strong acid with a weak base; a weak base with a weak acid; and a weak acid with a weak base, and compared the errors. For a proper choice of an indicator, the following conclusions are reached. If a strong base is used to neutralize a strong acid in concns. of 0.1  $N$  or above, any indicator that changes the color between  $pH$  5-10 can be used. In 0.01  $N$  concns.,  $m$ -nitrophenol, or neutral red is best. If a strong base is used to neutralize a weak acid, an indicator that changes around  $pH$  8 such as phenolphthalein is the best, and the same is true when a strong base is neutralized with a weak acid. If a weak base is to be neutralized with a strong acid, or a strong acid with a weak base, such an indicator as hematoxylin, methyl red or Congo red gives the best result. In neutralization of a weak acid with a weak base, or a weak base with a weak acid, a choice of an indicator depends on the dissociation const. of the acid and the base. If  $\text{NH}_3$  and  $\text{AcOH}$ , which have about the same dissociation const., neutral red or  $m$ -nitrophenol that change color around  $pH$  7 is the best. S. T.

The salt error of indicators in solutions poor in electrolytes. I. M. KOLTHOFF. *Rec. trav. chim.* 44, 275-8(1925).—It is known that salts exercise an influence on the equil. between the acid and basic form of a dye indicator. It is assumed in this case that the  $H_1$  electrode gives the correct values and the difference in the electrometric and colorimetric detns. expressed in  $pH$  is called the salt error of the indicator. Generally this salt error has been detd. at high salt concns. and it is assumed that at low concns. of salts the error is negligible. This is not true. Since the potentiometric method is not so useful in solns. poor in electrolytes as the colorimetric method, K. has detd. the salt error for about 14 common colorimetric indicators. These errors are smallest for  $\alpha$ -naphthol blue, cresol red, neutral red, bromothymol blue, bromocresol purple, methyl red and methyl orange.

E. J. WITZEMANN

A new method of quantitative analysis by means of X-rays. E. DELAUNEY. *Compt. rend.* 180, 1658-61; *Recherches et inventions* 7, 597-602(1925).—Different elements show different absorption coefficients of monochromatic X-rays. The following relation holds:  $I = I_0 e^{-am}$  in which  $I_0$  is the value for pure water,  $I$  for the soln.,  $a$  is a characteristic for the element in question and  $m$  represents g. of substance per cc. of soln. Details are given showing how solns. of  $BaCl_2$  and  $SrCl_2$  can be analyzed for Ba and Sr, of KBr and KCl for Cl and Br and of KI and KBr for I and Br with a relative error of less than 1%.

W. T. H.

Induced crystallization in microchemistry. Application to the diagnosis of certain sugars and polyalcohols. G. DENIGES. *Microchemie* 3, 33-7(1925).—Crystn. has often been brought about on a large scale by inoculation but the principle has not been applied very often to chem. detns. In this interesting paper it is shown how, with 0.1-0.3 mg. of substance dissolved in a drop of water, it is possible to induce crystn. of a desired substance by stirring the gelatinous mass (formed by evapn.) with a rod which has touched a crystal of the pure substance. Then, by extg. the cryst. mass with a mixt. of equal parts acetone and  $AcOH$ , and recrystg., it is possible to obtain crystals which can be identified under the microscope. Various disaccharides and polyhydric alcs. have responded successfully to this treatment.

W. T. H.

Microdetermination of chloride, bromide and iodide in the presence of one another. R. SYREBINGER AND I. POLLAK. *Microchemie* 3, 38-59(1925).—The sepn. of  $I^-$  from  $Cl^-$  and  $Br^-$  by means of  $TiCl_3$  proved unsatisfactory when the ppt. of  $TiI_3$  weighed less than 20 mg. Pptn. of  $PdI_2$  proved more satisfactory and serves for the detn. of  $I^-$  either alone or in the presence of other halides. The electrolytic formation of Ag halide on a Ag anode proved inaccurate, but from 3-4% KCN solns. to which a little KOH has been added it was found possible to deposit Ag quant. from solns. of Ag halide in KCN, but care must be taken to prevent oxidation of the cathode deposit. When  $Cl^-$ ,  $Br^-$ , and  $I^-$  are present together, it is best to ppt.  $PdI_2$  for the  $I^-$  detn. and in another sample det. the wt. of ppt. produced by  $Ag^+$  and the Ag content of the ppt. by means of electrolysis. Careful attention to numerous details is important.

W. T. H.

Separation of iron, aluminium, chromium and phosphoric acid from zinc, nickel, cobalt and manganese and determination of the latter. K. K. JÄRVINEN. *Z. anal. Chem.* 66, 81-100(1925).—The solns. used in nearly all of the expts. described contained 0.5 g. of Fe and 0.1 g. each of Al, Cr, P, Zn, Ni, Co and Mn in 100 cc. Not more than  $\frac{1}{4}$  as much P as Fe, Cr and Al should be present. If sufficient  $H_2SO_4$  is not already present, add 2 g. of  $(NH_4)_2SO_4$  and neutralize with 2 N  $(NH_4)_2CO_3$  until a distinct, permanent turbidity is obtained in the cold. Boil this neutralized soln. until practically all of the  $Fe^{+++}$  is pptd. as basic sulfate. To the hot soln. add sufficient Na or  $NH_4$  nitrate. For 1 g. of Fe use 3.5 g., for 1 g. Al, 7.5 g. and for 1 g. Cr, 4 g. of  $NH_4NO_3$ . Shake and without further boiling allow the soln. to stand for 15 mins. This causes complete pptn. of all Fe, Cr, Al and P. Shake well, make up to 200 cc. in a calibrated flask, filter and use 100 cc. of the filtrate. For the sepn. of the Zn, Ni, Co and Mn, the method described by F. P. Treadwell in his textbook is recommended with slight modifications. The ppts. of  $ZnS$  and of  $NiS$  and  $CoS$  are slightly impure and for the most accurate work should be examd. for impurities. The above method of sepg. the trivalent from bivalent metals appears to be more satisfactory than the conventional basic acetate or  $BaCO_3$  methods. It can be used to advantage in the analysis of Zn ores and is better than the common method of removing Fe and Mn by  $NH_4OH$  and  $Br_2$ . For the detn. of small quantities of adsorbed Mn, Ni and Co, colorimetric methods are recommended in which Mn is converted to  $MnO_4^{2-}$ , Ni to colloidal sulfide and Co to thiocyanate. W. T. H.

Determination of potassium by the perchlorate method. A. VÖRNER. *Chem. Weekblad* 22, 138-40(1925).—The results for fertilizer analysis are nearly theoretical;  $KClO_4$  is insol. in 96% alc., contg. 0.2-0.3%  $HClO_4$ . A little Ba is harmless but large

quantities of sulfate have to be removed with Ca. The evapn. of the salt-mass with HClO must be continued without interruption until no more vapors are evolved.

B. J. C. VAN DER HOEVEN

**Polarimetric determination of inactive substances:** potassium. A. WRÓBEL. *Roczniki Chem.* 4, 287-94(1924).—When a soln. contg. Na H tartrate and  $\text{NH}_4$  molybdate is treated with a K salt, the reaction of the latter with the tartrate results in depression of the optical rotation of the liquid, the extent of this depression serving as a means of detg. the amt. of K used.

B. C. A.

**Determination of copper by rapid electrolysis in the presence of tin, antimony and lead.** J. LUKAS AND A. JILEK. *Chem. Listy* 18, 378-83(1924).—For the sepn. of Cu from Sn by rapid electrolysis, the sample is dissolved in a mixt. of  $\text{HNO}_3$  and tartaric acids and the soln. electrolyzed in a Pt dish, which serves as cathode, using a rotating anode. If Sb is present HF and phosphoric acid must also be added; in neither case does the presence of Pb affect the results. The first Cu deposit should be redissolved in  $\text{HNO}_3$  and the soln. filtered and electrolyzed again to remove traces of C and Sb.

B. C. A.

**The determination of zinc in aluminium.** MAX SCHMIDT. *Metall u. Erz* 22, 77-8(1925).—Zn generally occurs in com. Al to the extent of 0.01 to 0.04% and is difficult to det. Ordinary  $\text{H}_2\text{S}$  and electrolytic pptn. are not satisfactory. The method given uses 10 g. Al dissolved in 150 cc. of 30% NaOH, and made up to 400 cc. Filter, warm and add  $\text{Na}_2\text{S}$  soln. Filter and dissolve the ppt. in HCl, neutralize with  $(\text{NH}_4)_2\text{CO}_3$ , add 3 cc.  $\text{NH}_4\text{OH}$  and 6 g. monochloroacetic acid. Warm, add 6-8 drops of 20%  $\text{Na}_2\text{SO}_4$  soln. and pass in  $\text{H}_2\text{S}$  for 30 min. The colloidal S causes pptn. of the ZnS in a filterable form. Wash the ppt. with 1%  $\text{NH}_4\text{NO}_3$  soln., ignite and weigh as  $\text{ZnO}$ .

C. G. KING

**Method of assay for osmiridium in pyritic concentrates.** F. W. WATSON. *J. Chem. Met. Soc. S. Africa* 24, 185-6, 268-71(1924).—For a concentrate contg. over 0.5 oz. Os-Ir per ton, use a 200-g. sample and more for lower-grade ores. Add this slowly to 800 cc. of warm 8 N  $\text{HNO}_3$  in a 4-l. beaker, adding a few Fe turnings to start the reaction if necessary; after action has ceased fill the beaker with  $\text{H}_2\text{O}$ , let stand, decant, warm the residue with a little concd.  $\text{HNO}_3$ , dil. and decant again, and treat with HCl- $\text{HNO}_3$  till all the Au is dissolved. Wash the insol. matter into a 400-cc. beaker and "jig" off the sand, re-washing all sand removed. Fuse the residue with  $\text{KHSO}_4$  to attack Cr and Ti minerals, treat the melt with dil. HCl. Remove the  $\text{ZrO}_2$  by careful "jigging," and weigh the residual Os-Ir as such. Panning a 25-50-lb. sample down to a final concentrate of 50 g. before treatment with  $\text{HNO}_3$  is recommended.

WM. B. PLUMMER

**Determination of antimony, with reference to the note of A. Ecke.** V. AUGER. *Ann. chim. anal. chim. appl.* 7, 100-1(1925); cf. C. A. 18, 3157.—E. proposed detg. Sb in an alloy by dissolving in a mixt. of HCl and  $\text{CuSO}_4$  and titrating with  $\text{KMnO}_4$ . The inaccuracy of such a method is pointed out. E. also proposed detg. Sb iodometrically in the presence of Cu in a soln. contg. Cu. If much Cu is present such a method is very unsatisfactory.

W. T. H.

**Determination of small amounts of boron in tungsten.** DOROTHY H. BROPHY. *J. Am. Chem. Soc.* 47, 2856-61(1925).—Fuse 0.3-0.5 g. of metal with 0.5-0.7 g.  $\text{NaNO}_3$  and 1.5-3 g. of NaCl. Leach the melt with 30 cc. of water, add 2 g. solid  $\text{Ba(OH)}_2$  and heat to boiling. Filter out of contact with  $\text{CO}_2$ . Add methyl orange indicator and a little KI. Make acid with 6 N HCl and allow 1 min. for the reduction of nitrite. Add  $\text{Na}_2\text{S}_2\text{O}_5$  to react with liberated  $\text{I}_2$  and introduce a current of  $\text{CO}_2$ , free air to remove NO. Neutralize carefully and titrate the  $\text{H}_3\text{BO}_3$  in the usual way with phenolphthalein as indicator in the presence of glycerol or mannitol. Instead of fusing with  $\text{NaNO}_3$  and NaCl, NaOH and  $\text{Na}_2\text{O}_2$  can be used. The treatment with KI is then unnecessary but the manipulation is on the whole more difficult.

W. T. H.

**Determination of vanadium in ferrovanadium and the red-green method.** KOCH. *Chem.-Ztg.* 49, 479-80(1925).—Dissolve 0.2 g. of Fe-V in  $\text{HNO}_3$  or aqua regia, evap. to fumes with 15 cc. of  $\text{H}_2\text{SO}_4$ , dil. to 250 cc. and carefully oxidize with  $\text{KMnO}_4$ . Dil. to 1.5 l., add 10 cc. more of  $\text{H}_2\text{SO}_4$  and an excess of standard  $\text{FeSO}_4$  soln. Titrate the excess  $\text{FeSO}_4$  with  $\text{K}_2\text{Cr}_2\text{O}_7$  using a soln. of diphenylcarbazide in AcOH as indicator.

W. T. H.

**New reactions for nitrate and nitrite.** II. S. VÁGL. *Z. anal. Chem.* 66, 101-4(1925); cf. C. A. 19, 2000.—Pyrogallol or pyrocatechol can be used for the colorimetric detn. of 0.5-1 mg. of nitrite. Five cc. of a 1% soln. in 50% AcOH should be used for 40 cc. of aq. soln.; reddish brown colorations are obtained which become yellowish on standing when pyrogallol is used. Nitrates give no color. Hydroquinol in 50%

at the beginning of the distn. with HCl and is often found in relatively large quantities in 360 cc. of distillate obtained with properly controlled temp. If the total yield of the condensed phloroglucide, insol. in alc. after drying or after pptn. in hot solu., is, in such cases, taken as a basis for computing the pentosan content, the results are too high. In order to obtain approx. correct results in the pentosan detn. by the phloroglucinol method, the distn. should only be continued until the pentosans are just decomposed and this is usually accomplished when 150-180 cc. of distillate have been obtained. The progress of the decompn. can be followed by means of the phloroglucinol-HCl test; if the distillate contains more than a trace of furaldehyde, the ppt. has a greenish cast. The condensation with phloroglucinol should take place at room temp. and the ppt. be extd. with alc. The pentosan content obtained from phloroglucide dried prior to the extn. represents the max. possible value and that obtained after extg. the undried ppt. with alc. practically represents the min. possible value. An absolutely accurate analysis of substances which are not fairly pure pentoses or pentosans cannot be accomplished by means of the phloroglucinol method. The accurate detn. of the content of methylpentosan is also impossible by means of this method.

W. T. H.

Tariff for the analysis of foods, agricultural products, natural substances and industrial products, minerals and metallurgical products, fuels and chemical products. AXON, *Ann. chim. anal. chim. appl.* 7, 67-75, 101-8 (1925).—The French chemists have adopted standard charges and specified the appropriate wts or vols for all the common materials which are likely to be submitted for chem. analysis. W. T. H.

DUPARC, LOUIS and BASADONNA, M. *Manuel théorique et pratique d'analyse volumétrique*. 2nd ed. revised and enlarged by L. Duparc and Paul Wenger. Paris: Payot, 214 pp. Fr 18

KONINCK, L. L. DE *Manipulations chimiques qualitatives et quantitatives prépar. à l'étude systém. de l'analyse*. 6th ed., published by M. Huybrechts. Paris: Ch. Béranger, 195 pp. Fr 18

## 8—MINERALOGICAL AND GEOLOGICAL CHEMISTRY

EDGARY WHERRY

Pufahlite, a new sulfostannate. AHLFELD, *Metall u. Erz* 22, 135-6 (1925).—A preliminary note on a new mineral having the compn. Sn 41.9, Pb 37.4, Zn 6.3, S 13.5%, and Ag 208 g. per ton. It has metallic luster, resembles molybdenite and gives a black streak, its hardness = 2-3,  $d = 5.4$ , occurs in opaque, thin leaflets having a rhombic or monoclinic form.

C. G. KING

Micrographic examination of the structure of clays. BEATRAN, *Recherches et inventions* 4, 825-33, 841-51 (1923).—True mica does not occur frequently in clays, and the presence of alkalies must be attributed to some other mineral. As he cannot identify microscopically any such mineral, B. concludes that the alkalies were absorbed when they were liberated by the disintegration of the feldspars from which the clays were produced.

A. PAPINEAU-COUTURE

The system sodium nitrate-sodium sulfate-water, and the minerals darapskite and nitroglauherite. H. W. FOOTE, *Am. J. Sci.* 9, 441-7 (1925).—Mixts. in varying proportions of recrystd.  $\text{NaNO}_3$  and  $\text{Na}_2\text{SO}_4$  and water were shaken in a thermostat until equil. was reached, when the mixts. were filtered through glass wool and the filtrates and residues were analyzed to det. the proportions of the original salts in each. This was done for 2 temps., 25° and 35°. The only double salt found in this study was  $\text{NaNO}_3 \cdot \text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ , the same as darapskite, which occurs in Chili. The results also show that the alleged mineral nitroglauherite does not exist, the mineral thought to be a new species being a mixt. of darapskite and  $\text{NaNO}_3$ . The soly. results at different temps. are illustrated by a solid diagram which is described at length.

L. W. RIGGS

A new meteorite from Baldwin, Mississippi. L. C. GLENN, *Am. J. Sci.* 9, 488 (1925). cf. Merrill, *C. A.* 19, 2318

L. W. RIGGS

Geology and ore deposits of the Aravaipa and Stanley mining districts, Arizona. C. P. ROSS, U. S. Geol. Survey, *Bull.* 763, 117 pp (1925).—Deposits of Au, Ag, Pb, Zn, Cu and coal are described.

L. W. RIGGS

Melrose phosphate field, Montana. R. W. RICHARDS and J. T. PARNER, U. S. Geol. Survey, *Bull.* 780A, 1-32 (1925).—Extensive beds of phosphate rock, carrying over 60% of "bone phosphate," are described. Deposits of Au, Ag, Pb and Cu are found in this area.

L. W. RIGGS

Origin of the hoghead coals. REINHARDT THIESSEN. U. S. Geol. Survey, *Professional Paper* 132-I, 121-38(1925).—According to origin bituminous shales and cannel coals may be classified into humic, spore, ceric, resinous and algal deposits. The yellow bodies of the hoghead coals represent alga-like organisms heretofore not well known. These organisms are similar to one living in salt lakes in S. Australia, which is named *Elaeophyton* because of the large amt. of oil it contains. Colonies of this organism appear on the lakes toward the end of winter and are blown to the shore where they form a rubber-like mass called coörongite which is rich in oil and volatile matter. When heated coörongite melts and burns with a bright hot flame. It appears to be the peat stage of hoghead coal. Analysis of coörongite gave: moisture 16, volatile matter 90.1, fixed C 26, ash 5.7%. Ultimate analysis gave H 11.3, C 73.8, N 0.7, O 8.4, S 0.1, ash 5.7%. It is partly sol in  $CS_2$ ,  $CHCl_3$ ,  $Et_2O$  and  $C_6H_6$ . L. W. RIGGS

The occurrence of crystalline paraffin in a Styrian brown coal from the inner-Alpine Miocene. M. DOLCH *Braunkohle* 24, 218-21(1925).—White inclusions observed were 1-2 mm.  $\times$  several mm., and on mechanical removal and testing sintered shortly before melting, were fluid at 73.5°, and were apparently cryst. paraffin. Larger amts. were obtained by reflux extr. with benzene at 56° followed by crystn. from acetone, the product, m 73.1°, microanalysis showing C 86.41, H 13.19, ash 1.32%, the latter due to microscopic coal particles. It is of interest to note that the primary tar obtained by low-temp. carbonization of this coal contained only a small amt. of solid paraffins, they having apparently undergone decomposition. WM B. PLUMMER

The geological, technical and economical situation of the oilfields of South-Roumania. W. KAUNHOWEN. *Glückauf* 61, 324-34, 364-9(1925) OSCAR PAUK

Petroleum in France, its origin and its discovery. HENRI CHARPENTIER. *Rev. ind. minérale* 1925, 199-220. C. C. DAVIS

Shonkinite related to granite. F. F. GROVE *Am. J. Sci.* 9, 472-80(1925).—The shonkinites (of the Basswood type) from Minn. and Mont. were the subjects of critical petrographic study. A sample from Giant's Range, Minn., was analyzed by S. Allison with the following results:  $SiO_2$  49.65,  $Al_2O_3$  9.27,  $Fe_2O_3$  5.00,  $FeO$  6.08,  $MgO$  8.89,  $CaO$  13.08,  $Na_2O$  2.38,  $K_2O$  1.71,  $H_2O$  +1.71,  $H_2O$  -0.28,  $TiO_2$  0.80,  $ZrO_2$  0.05,  $P_2O_5$  0.06,  $Cr_2O_3$  0.04,  $MnO$  0.56,  $SrO$  0.12,  $BaO$  0.16, sum 90.93%; sp. gr. = 3.000. L. W. RIGGS

Erosion by solution and fill. W. T. LEE. U. S. Geol. Survey, *Bull.* 760C, 107-21 (1925).—Pecos Valley in SE New Mexico is a succession of broad shallow depressions which appear to be caused mainly by local subsidence due to the removal by soln. of sol. rock near the surface. The insol surface material is washed into subterranean caverns by water which dissolves the sol. rocks and forms other caverns. L. W. R.

COLE, GRENVILLE A. J. and HALLISSY, T.: *Handbook of the Geology of Ireland*. Preface by John W. Evans. London. T. Murby. 90 pp. 8s. 6d.

DUSSET, M.: *Les gisements algériens de phosphate de chaux*. Paris: Dunod. 300 pp. Fr. 25.

Handbuch der Mineralchemie. Vol. 4. Dresden: Th. Steinkopff. R. M. 7.50. Cf. C. A. 19, 1393.

LAUBMANN, HEINRICH: *Die Mineralagerstätten von Bayern r. d. Rh.* Munich: Piloty & Loehle. 111 pp. R. M. 8.50.

## 9—METALLURGY AND METALLOGRAPHY

D. J. DEMOREST, & S. WILLIAMS

Gold, silver, copper, lead and zinc in the Eastern States in 1924. J. P. DUNLOP. U. S. Geol. Survey, *Mineral Resources of U. S. 1924*, Part 1, 1-6 (preprint No. 1, published June, 1925). E. H.

Principles of metallurgy of ferrous metals for mechanical engineers. III. Determination of the properties of metals. LEON CAMMEN. *Mech. Eng.* 47, 559-65 (1925); cf. C. A. 19, 2183. E. H.

Metallurgical treatment of zinc-retort residues. B. M. O'HARRA. *Bur. Mines Tech. Paper* 341, 23 pp. (1925).—Final report; cf. C. A. 17, 2550. A bibliography is appended. A. BUTTS

Floating and leaching copper-molybdenum ores. H. A. DOERNER. *Eng. Mining J.-Press* 119, 925-6(1925).—Most Mo ores contain Cu, which must be cut to <1% in the concentrates to make them salable, and even smaller amts. are penalized. D.

outlines the exptl. development of a process of selective flotation followed by leaching with  $\text{Fe}_2(\text{SO}_4)_3$ , which recovers over 85% of the  $\text{MoS}_2$  in a high-grade product free from Cu, and over 85% of the Cu in a concentrate of 35% Cu, from a typical ore carrying 3%  $\text{MoS}_2$  and 3.2% Cu.  $\text{MoS}_2$  is first floated in a fairly clean concentrate, with kerosene as a reagent. The concentrate is then cleaned by a second flotation, with  $\text{SO}_2$  to inhibit the floating of Cu. The resulting concentrate carrying about 1.5% Cu is leached by percolation with hot  $\text{Fe}_2(\text{SO}_4)_3$  soln. Cu is dissolved completely and Mo is unattacked. The soln is regenerated by pptg. the Cu on scrap Fe and treating with  $\text{SO}_2$  and air in oxidizing cells. The leaching cycle is continuous. This process will cause the presence of Cu in a Mo ore to increase the value of the ore. A. BUTTS

The Golden Cycle "superthickener" and clarifier. NOEL CUNNINGHAM. *Eng. Mining J.-Press* 119, 905-7 (1925).—A new type of thickener invented by H. S. Cœ and perfected by A. L. Blomfield at the Golden Cycle cyanide mill, Colorado Springs, is described, with discussion of results obtained during 2 years' trial of a full size unit. Its action is to lower or draw down in the tank the level of the thickening zone, thus greatly increasing the settling rate of solids, and to de-water and compact the bottom layer of settled solids. This is accomplished by providing a bottom porous only to the liquid in which the solids are suspended, and mechanical means for cleaning the surface of this bottom so as to maintain a permeable filter medium. Examples are given of its application in cyaniding and its use as a clarifier. It yields a crystal-clear Au soln. at a high rate of speed. A. BUTTS

Influence of certain solids and gases on the chloridization roast. A. B. BAGDASARIAN. *Eng. Mining J.-Press* 119, 962-4 (1925).—A discussion of the principal reactions in chloridizing, roasting and chloride volatilization, especially from the standpoint of chem. equil. It is concluded that O, S and  $\text{H}_2\text{O}$  are beneficial during chloridization, but harmful during the period of volatilization of the base-metal chlorides.  $\text{SiO}_2$  is always beneficial and may be added to eliminate the harmful decomposing effects of CaO on base-metal chlorides. A. BUTTS

Recent development in the fine grinding and treatment of Witwatersrand (gold) ore. C. R. DAVIS, J. L. WILLBY AND S. E. T. EWING. *Trans. Am. Inst. Min. Met. Eng.* Dec., 1924, 22 pp.—A series of tests is described designed to discover the most efficient and economical method of reducing Rand banket ore to a suitable size for treatment. By feeding comparatively coarse material to the tube mills it was found possible to eliminate the use of stamp batteries and of amalgamating plates. The run-of-mine ore is broken directly in gyratory crushers or rolls to 1-1½ in. pieces, and this material is fed direct to the tube-mill together with about 20% of uncrushed ore which serves as a grinding material. The discharge from the mill is screened on a 90 mesh sieve, and the undersize, over 60% of which will pass a 200-mesh sieve, is passed to a Dorr thickener, then to the cyaniding plant. The oversize, consisting chiefly of worn and rounded pebbles, is re-crushed with further quantities of ore. The output of a mill averages 140 tons of slimes per day, while about 12 tons of pebbles are produced. By this process an extra recovery of 0.20 dwt. of gold per ton is effected with a saving of 5d. per ton in the costs. Details are given of the working of the process at the Spring Mines, together with a considerable amt. of cost data. B. C. A.

Reduction of iron ores by carbon monoxide. H. KAMURA. *Trans. Am. Inst. Min. Met. Eng.*, Feb., 1925 (advance copy) 16 pp.—The proper temp. for the reduction of Fe ores by CO depends on the chem. and phys. properties of the ore. Magnetite requires a slightly higher temp. than limonite or hematite ores. The time required for reduction increases with the d. and also with the degree of crystn. of the ore. In lab. expts on the reduction of Japanese hematites, ore 1 in. in size was reduced in 3½-5 hrs., and ore under ½ in. in size in 2-3 hrs., at a temp. of 900°. The possibility of the direct reduction of ore to spongy Fe at comparatively low temp. and the melting to steel without decarburizing is discussed. B. C. A.

Production of copper in the mining district of Kvarzhana (Transcaucasus). SIMONOVICH. *Rev. universelle mines* [7] 6, 279-91 (1925).—The methods of exploitation are described and illustrated, with analyses of the ores. The chief ore is chalcopryrite which contains 3.5-12.5% Cu, the content usually being 5-8%. The general scheme of production is pyritic fusion which gives a mat contg. 36-45% Cu, treatment in basic converters to black Cu and refining of the Cu in an oil-heated furnace. C. C. DAVIS

Concentration in the Tri-state district. C. O. ANDERSON. *Bull. Am. Zinc Inst.* 8, No. 5, 82-98 (1925).—A general discussion of concn. in this district. Milling is primarily for sepg. the blende and the *shint*. The 2 great sources of loss in blende are in the locked grain, called "chats," and in slime. Each of these is described as to (1) its isolation from other mill products, and (2) its subsequent treatment after isolation.

While the "chats" and slimes receive most consideration in the paper they are discussed in connection with the jig room, the sludge room and the flotation dept. Mill tailing losses have been reduced  $\frac{1}{4}$  by observation of the improved operation features outlined.

W. H. BOYNTON

The manufacture of pure tungsten. G. A. PERCIVAL. *World Power* 4, 11-9 (1925).—A review

C. G. F.

Notes on Western lead smelters. A. B. PARSONS. *Eng. Mining J.-Press* 119, 876-83(1925).—Recent tendencies in improved practice are classified as: (1) more mechanical handling, (2) improved roasting, with more ZnS to be eliminated; (3) greater recovery from smoke, with baghouses, improved Cottrell app., and special by-product plants. New equipment and practice at many of the smelters are described.

A. BURTS

The El Paso smelter. G. J. YOUNG. *Eng. Mining J.-Press* 119, 1041-7(1925).—A description of the lead and copper plant of the American Smelting and Refining Co.

E. H.

Recent views of blast furnace functions. DANIEL SILLARS. *J. West. Scot. Iron & Steel Inst.* 32, 52-9(1925).—A brief résumé of iron-working and a discussion of views as to the manner in which fuel is consumed in the modern blast furnace employing coke or coal. To secure the thermal advantage of indirect reduction it must take place at a temp. lower than that at which the soln. of C becomes appreciable to insure that the CO formed passes away at the top of the furnace unchanged. Indirect reduction possesses the mech. advantage of being a gaseous reaction. Cokes otherwise suitable for metallurgical uses do not differ sufficiently in their apparent d., porosity or character of carbonaceous matter to influence to any degree the extent of the combustion zone. Several diagrams of flow of stock under varying combustion conditions are shown.

W. H. BOYNTON

Combustion of coke at the tuyère level of the blast furnace. S. P. KINNEY. *Blast Furnace & Steel Plant* 13, 243-7(1925).—Exptl. results show that the extent of penetration of the combustion zone at the tuyère level of the blast furnace is a const. not dependent upon the amt. of air blown. The furnaces, method of obtaining the gas samples, and the app. employed are described.

W. H. BOYNTON

A study of carbon used in blast furnace otherwise than before the tuyères. W. D. BROWN. *Blast Furnace & Steel Plant* 13, 236-8(1925).—B studies the wt. of C used other than at the tuyères. The C thus used may be classed as follows: (A) reduction of Si, Mn, P and S, (B) reduction of last traces of Fe oxide, (C) impregnation of pig Fe; (D) "soln. loss", (E) decompn. of water. The method of calcn. of C burnt before the tuyères, the wt. of CO<sub>2</sub> in top gases, and the limits of error in the table shown are outlined. The C used otherwise than at the tuyères may be in error in lbs./ton pig iron: (1) in coke screened out 10; (2) C in flue dust about 0.6% 12; (3) C in coke, due to moisture, 3%, 10; (4) CO<sub>2</sub> 0.5% low in gas analysis—30; (5) increase of 1 grain moisture in blast 10. B concludes that the C used otherwise than at tuyères is more than the sum of that required for reduction of metalloids, for impregnation, and "soln. loss" equal to the C in the stone. The CO<sub>2</sub> is generally less than that resulting from the reduction by CO, showing the "soln. loss" has occurred and that it is more than equal to the C in the limestone. Fe is reduced in the top of the furnace by CO but the CO<sub>2</sub> resulting and the CO<sub>2</sub> from limestone cause soln. loss.

W. H. BOYNTON

Power generation by blast furnace plant. O. C. CALLOW. *Iron and Steel Eng.* 2, 212-6(1925).—C shows how blast furnace gas is used under boilers to produce steam, also how coke breeze may be used where boilers are equipped with mech. stokers and forced draft. The marketing of the surplus power produced by a single-isolated furnace is discussed and the advantage of having 2 furnaces operating, thereby reducing the no. of low-steam periods, is pointed out. A better rate per kw. would then be possible, because the utility company would not have to hold their equipment in reserve to pick up the load.

W. H. BOYNTON

The automatic blast furnace. F. W. CRAMER. *Iron and Steel Eng.* 2, 229-42 (1925).—C. describes the operation of the one-man elec. charging arrangement at the Johnstown, Pa., plant of the Bethlehem Steel Co. Many advantages are claimed for this arrangement. Indicating recorders can be arranged to show in detail the different operations. Given the output of any furnace and the material involved, the entire operation can be worked on a detailed schedule component parts of which are the time taken by the travel of the skip and the operation of the distributor and large and small bells. Another advantage is the proper distribution regardless of the size of the charging units. Several illustrations and a discussion are included.

W. H. BOYNTON

Furnace lining wears unevenly. S. P. KINNEY. *Iron Age* 115, 1639-40(1925).—

Results are given of tests made on a 300-ton Fe blast-furnace to det. the thickness of the lining and the temp gradient in the lining. Holes were drilled at 4 points and a thermocouple was inserted at intervals. Nineteen ft. above the tuyeres a 40.5 in. lining had corroded away 14.5 in.; 42 ft. above, 8.5 in.; 53 ft. above, none; and 60 ft. above (just below the armor plate), 12.5 in. The temp gradient could be used to det. the condition of a lining and its probable life. A. BUTTS

The occurrence of alkali cyanides in the iron blast-furnace. S. P. KINNEY AND E. W. GUERNSEY. *Ind. Eng. Chem.* 17, 670-4 (1925).—Detns. were made of the concn. of total alkali and of alkali cyanides at various levels in a 300-ton furnace and at various distances from the wall. Cyanide concn., figured as KCN, was from 0 to 4 g. per cu. m. of gas. If  $1/10$  of the furnace gas were withdrawn continuously from the level of max. concn., it should yield 690 kg. of KCN daily. A sample of fume from this level analyzed 31% KCN, 25  $K_2CO_3$ , 18 ZnO, 12 PbO. Such concn. is due to accumulation by repeated vaporization below and condensation above. Fume from the slag notch was 46% KCN and 14 NaCN. The total alkali content of the charge was 0.51%  $K_2O$  equiv. of this  $1/4$  leaves the furnace in the slag and  $1/4$  in the top gases. A. BUTTS

Open-hearth pressure control. G. R. MCDERMOTT. *Blast Furnace & Steel Plant* 13, 230-3 (1925).—Introduction of a steam turbine blower with a const. vol. governor on a gas producer which supplies gas to an open hearth furnace has resulted in a 30% saving in the steam required for blowing the producers and an increase in the steel produced by the furnace and a corresponding reduction in coal used per ton of steel produced. Several charts, curves and illustrations are shown. W. H. BOYNTON

Gas reactions in the regenerators of an open-hearth furnace fired with a mixture of blast-furnace and coke-oven gas. W. HÖLSARTH. *Mitt. Versuchsanstalt Deutsch-Luxemburgische Bergw. u. Hütten A.-G. Dortmund* 1, 131-52 (1924).—The preheating of the gas-mixt. in the regenerators results in an increase of the H and CO content of the gases and in the deposition of part of the C. This action is dependent upon the temp., on the time of passage of the gas through the regenerator, and on the compn. of the gas. At 1000-1100° a longer time in the regenerator results in an increase of 15-18% in the calorific power of the gases, due to an increase in their latent heat, and part of the C first deposited is once again converted into CO. B. C. A.

Study of a regenerative, continuous heating furnace. G. NEUMANN. *Stahl u. Eisen* 44, 1011-9 (1924).—Besides gas analysis at various places, there were measured the steel charged, the temp. in the furnace, temp. of billets (in the furnace and after removal), temp. in gas- and air-chambers and valves. Blast furnace gas was the fuel. Loss by scaling was measured; it depends more on time and temp. than on completeness of combustion (i. e., neutral or reducing flame). Certain amts. of  $H_2O$  and  $CO_2$  were always present. At high temp. these oxidize; if the temp. be lowered by admixing air, the temp. gradient of the gases is less steep, i. e., the hot end is cooler and the cool end hotter than before; but the steel absorbs a given amt. of heat during which period (above a certain min. temp.) it scales. The hot flame zone should not have over 2% CO for correct flame. It is suggested that the heat loss in skids be reduced by placing over them removable castings which latter are to be allowed to reach, say, 500°. It is recommended that air be preheated to 1000°, gas to 900°; other data are not of very general interest. A. HUNGELMANN

Recovery of heat lost in the Martin furnace. PIERRE KERSTEN. *Rev. universelle mines* [7] 6, 144-59 (1925).—A detailed discussion, with quant. data, of the heat lost by radiation, by convection and in the chimney, the advantages and disadvantages of a boiler with forced draft, the principles governing the type of boiler to be adopted and the results of tests on a typical installation with a 30-ton furnace. The latter tests show the amts. and compn. of the fuel and gases, the boiler output based on the fuel consumed in the gas producer, the heat losses and the thermal balance. C. C. DAVIS

Substitution of anthracite for pig iron in Martin furnaces. N. RONZÉVIRCH. *Messageur et métaux Russe* 1923, Nos. 4-8, 60-5 (April-Aug.); *Rev. métal.* 22 (Extraits), 231-2 (1925); cf. Troubine, *C. A.* 18, 3025.—At the Poutiloff plant when most or all of the pig Fe was replaced by anthracite, approx. twice as much C had to be added in the latter form as in the form of pig Fe, the normal cycle of operations required approx. 15% more time with anthracite, elimination of P was perfect and elimination of S was satisfactory. The steels obtained with anthracite were of normal compn. and contained less P than when pig Fe was used. A. PAMNEAU-COUTURE

Efficiency of the Siemens-Marten furnace (open hearth). G. BULLE. *Stahl u. Eisen* 44, 1324-6 (1924).—Usually the efficiency is expressed by  $\eta = L/Q$ , L being the heat in a unit weight of steel (sensible heat from zero to m. p. plus heat of fusion plus sensible heat from melt to tapping temp.) and Q being heat consumption per unit weight

of steel. As the numerator is always about 300 to 350 a division of the values is desirable. This can be done by: metallurgical efficiency; furnace efficiency; gas producer efficiency (each being further divided). Examples are given. Control and improvements are made easier by this supervision. A. HUNGELMANN

Treating lead ashes in the reverberatory furnace. E. T. RICHARZ. *Metal Ind.* (London) 26, 575-6(1925).—A comparative discussion of advantages and disadvantages of blast furnace and reverberatory furnace treatment and an outline of certain rules in the latter treatment. The furnace should be preheated for 3-4 hrs. at about 650°, and dry ashes should be moistened to prevent excessive dusting, and several shovelful of powd. coke spread over the hearth just before charging. The amt. of coke charged with the ashes depends upon the PbO content. If time is needed it is charged after the ashes have become soft. It is not economy to force the Pb content of the slag below 40%, because of the unmarketability of slags with less Pb content. The conglomerate of slag and powder may easily be briquetted by coarse crushing, adding 6-7% water, mixing and pressing into briquets. These may be used in the blast furnace after being kept in a dry place about 2 weeks. W. H. BOYNTON

Melting pig iron in a cupola by means of charcoal. S. A. DAMOV. *Messageur ind. métaux Russe* 1924, Nos. 1-3, 102-9, *Rev. métal* 22 (Extraits), 231(1925).—On account of shortage of coke, the Oniejsky plant was forced to use charcoal, which was found inferior to coke both technically and economically. When charcoal must be used, it is advisable to add a certain proportion of coke, anthracite, or bituminous coal. A. PAPINEAU-COUTURE

Thermomagnetic analysis. Highly sensitive induction balance. P. NICOLAU. *Rev. métal*, 22, 273-90(1925).—N. gives a detailed description of a highly sensitive induction balance, and gives an example of its use for the study of a sample of piano wire. The results obtained are discussed and interpreted as indicating: on the one hand, progressive reconstitution of cementite, when drawing the temper up to 400°, by combination of the  $\alpha$ -Fe and C of the martensite, in the form of a solid soln; on the other hand, progressive decompn. of cementite by further drawing from 400° to the annealing temp., while the steel has a sorbitic structure. Existence of a max. cementite content at 400° when drawing the temper furnishes a satisfactory explanation of the variation observed at this temp. in the resilience of ordinary steels of the same nature as the piano wire, when quenched in water. A. PAPINEAU-COUTURE

$\beta$ -Iron and the specific heats of pure iron. A. BRODSKY. *Congrès de Leningrad* May-June, 1924; *Rev. métal*, 22 (Extraits), 206-9(1925).—From a discussion of the evidence on which is based the assumption of the existence of  $\beta$ -Fe, and from the results of extrapolations of A. Meuthen's observations (C. A. 7, 464-5), B. concludes that  $\beta$ -Fe does not exist, and that the existence of the point A<sub>1</sub> must be attributed to a formation which occurs in the system Fe-C (of a eutectic type) and of which nothing is known as yet. A. PAPINEAU-COUTURE

Carburization as a factor in the erosion of machine-gun barrels. W. W. DE SVESHNIKOFF. *Army Ordnance* 5, 794-7(1925). The cause of the white layer. HENRY PAY. *Ibid* 798-9. Erosion of machine-gun barrels. W. T. GORTON. *Ibid* 799. Additional tests needed to determine value of various steels. J. S. VANICK. *Ibid* 799-800. The nitrogen theory of erosion. H. E. WHEELER. *Ibid* 800-1. Old and new theories of erosion. A. G. ZIMMERMANN. *Ibid* 801-6. E. H.

Zinc coating. C. S. TREWIN. *Bull. Am. Zinc Inst.* 8, No. 5, 43-55(1925).—A description of the hot dip process as applied by hand dip, wire galvanizing and sheet galvanizing. Chem. tests, atm. tests and accelerated tests proposed and already applied are outlined. W. H. BOYNTON

Influence of Mn content on hydraulic properties of blast-furnace slag (GRUEN) 20. Strength and related properties of metals (ANON) 2. The equilibrium diagram of the system Fe-C-Ti (TAMARU) 2. X-ray examination of inner structure of strained metals (ONO) 2. X-ray analysis of electrolytic brass (NAKAMURA) 2. Relative value of CO and H as constituents of producer gas for Zn distillation furnaces (RICE) 21. Attaining high efficiency in industrial heating (HUFFELMANN) 21. An electrochemical method for estimating the corrosion of Fe and steel (BERRY) 4. The characteristics of refined Al from Grevenbroich (HOFFMAN, STAHL) 2.

CHAPLEY, A.: Tous les alliages. Env. 2500 formules de composition des alliages de toutes sortes. Paris: Gauthier-Villars & cie. 70 pp. Fr. 18.

MEHRTEHS, JOH.: Das Gusseisen. Seine Herstellung, Zusammensetzung, Eigenschaften u. Verwendung. Berlin: J. Springer. 66 pp. R. M. 1.50.

**Flotation.** O. B. D. LINDQUIST. Swed. 58,314, March 4, 1925. A certain quantity of kinetic energy is applied to the ore slurry, for instance, by means of a pump, which energy is later on utilized in injectors mounted in such a way that they will draw air and oil into the slurry.

**Reduction of ores by gases.** J. E. LEONARZ. Swed. 58,327, April 8, 1925. The gases used in the reduction are taken out and brought into contact with liquid metal in the presence of carbon and regenerated in this way they are again in full or in part utilized in the reduction process.

**Direct reduction of ore.** HORGANES BELLESHOLMS AKTIEBOLAG. Swed. 58,333, Feb. 25, 1925. The reduction is carried out in closed containers by heating to such high temps. that the charge will sinter together in one or more large lumps sufficiently coherent to be lifted out from the container without falling to pieces.

**Reduction of metal oxides.** D. W. BERLIN. Swed. 58,629, April 29, 1925. The oxides are mixed with Al-Si in a molten metal bath, where the mixt. is heated until reaction takes place.

**Production of zinc, lead, copper or their oxides from sulfidic ores or mats.** E. S. BERGLUND. Swed. 58,628, April 29, 1925. The materials are reduced without any preceding roasting or after an incomplete (not chloridizing) roasting. As a reducing agent is used a mixt. of  $\text{CaC}_2$  and  $\text{CaO}$  or  $\text{CaC}_2$  and  $\text{C}$  according to the O and S content of the ore or mat.

**Separating zinc and lead oxide from dust.** FINSFONGS METALLVERKS AKTIEBOLAG. Swed. 58,260, Feb. 18, 1925. The dust is given a vibratory motion of only a few mm. amplitude at a temp. above the m. p. of Zn, with the double purpose of agglomerating the metal particles and coincidentally sepg. the components according to their different sp. gravities.

**Chromium or manganese alloys low in carbon and silicon.** AKTIEBOLAGET FERROLEGERINGAR. Swed. 58,260, Feb. 25, 1925. The ore is reduced by a Si-Cr, or Si-Mn alloy with more than 10% of Si. This alloy is produced by reduction of the slag rich in Cr or Mn obtained by the reduction of the ore. Si or its alloy with Fe, Ca, Cr or Mn is used for the reduction of the slag.

## 10—ORGANIC CHEMISTRY

CHAS. A. RUTILLER AND CLARENCE J. WEST

**Liberation of hydrogen from carbon compounds.** J. V. E. DICKSON. *J. Am. Chem. Soc.* 47, 2061-2 (1925).—Fry, Schulze and Weitkamp (*C. A.* 18, 3357) apparently overlooked the work of Boswell and Dickson (*C. A.* 13, 320) on this subject. *C. J. W.*

**Stereochemistry and technics.** P. WALDEN. *Z. anorg. Chem.* 38, 429-39 (1925); cf. *C. A.* 19, 1125.—A thorough review of the history and the modern application of stereochemistry (asym. C atom) with biographical note on van't Hoff and le Bel.

J. T. STERN

**The hexabromide of diacetylene.** LESPIEAU AND C. PREVOST. *Compt. rend.* 180, 1347-9 (1925).—Noyes' hypothesis that the cryst. hexabromide,  $\text{C}_4\text{H}_2\text{Br}_6$  (I), obtained by the bromination of  $\text{C}_2\text{H}_2$ , occurs through the intermediate formation of small quantities of  $(\text{CH}=\text{C})_2$  (II), is substantiated by the formation of a hexabromide, m. 186.5°, when  $\text{Br}_2$  is added to II, in  $\text{CHCl}_3$  without cooling. This is identical in m. p. and cryst. form with the  $\text{C}_4\text{H}_2\text{Br}_6$  obtained by Willstätter by brominating 1,2-dibromo- and 1,1,2,2-tetrabromocyclobutane (III). I on treatment with Zn and EtOH regenerates II. It seems more probable that I is a straight-chain ethylenic compd., perhaps  $\text{CHBr}=\text{CBr}-\text{CBr}=\text{CHBr}$ , than that a ring should be opened by Zn and EtOH; accordingly I should be formed from III by a rupture of the ring.

I. P. ROLF

**Progressive halogenation of acyclic saturated hydrocarbons.** H. GAULT. *Rev. gén. sci.* 36, 26-75 (1925).—A critical review.

A. PAPINEAU-COUTURE

The glycol  $\text{CH}_2\text{C}(\text{OH})(\text{CH}_2\text{OH})$  LESPIEAU. *Compt. rend.* 180, 412-4 (1925); cf. *C. A.* 19, 813.—From 23 g. of  $\text{CH}_2\text{C}(\text{OH})(\text{CH}_2\text{Cl})$  (for the prepn. of which see earlier abstr.) in  $\text{Et}_2\text{O}$ , 8-9 g. of  $\text{CH}_2\text{C}(\text{OH})(\text{CH}_2\text{O})$  (I) is formed on addn. of anhyd

KOH. 1, b<sub>760</sub> 80-7°,  $d_{20}$  0.945,  $n_D^{20}$  1.427; it gives ppt. with  $\text{AgNO}_3$  or  $\text{NH}_4\text{CuCl}_2$ . By heating I with  $\text{H}_2\text{O}$  at 100° (sealed tube) for 20 hrs. 90-100% of  $\text{CH}_2\text{C}(\text{OH})(\text{CH}_2\text{OH})$  is formed; it m. 39.5-40.5°, its *diphenylurethan*, m. 133-4.5°, its *di-Br deriv.*, m. 47-8°; it does not give any ppt. with  $\text{AgNO}_3$  or  $\text{NH}_4\text{CuCl}_2$ , but may react to form sol. products.

WM. B. PLUMMER

**Preparation of alkyl sulfides.** A. E. WOOD. *J. Am. Chem. Soc.* 47, 2062(1925).—All the alkyl sulfides tested showed the presence of mercaptans; their complete removal may be accomplished by distg. the sulfides over finely divided Cu. Either the Cu mercaptide remains as a residue, or if heated to 125°, will decomp., giving CuS and the corresponding alkyl sulfide. C. J. WEST

**The action of nitrous acid on aliphatic primary amines and the existence of aliphatic diazo compounds.** J. BERK AND P. H. HERMANS. *Chem. Weekblad* 22, 270-2(1925).—Textbook data relative to the action of  $\text{HNO}_2$  on primary aliphatic amines are misleading. The replacement of  $\text{NH}_2$  by OH is actually a complicated side reaction. This is evident from the common transformation of cycloparaffin amines into rings with 1 more or 1 less C atom and of straight-chain primary amines into secondary or iso-als (Wallach, Demjanow, V. Meyer). The following reaction scheme explains the facts satisfactorily: an amine nitrite is formed and converted into a diazo compd. The terminal N of the latter is linked to the third (I) or to the second (II) C with subsequent elimination of  $\text{N}_2$  and addn. of  $\text{H}_2\text{O}$ . In I the original cycloparaffin ring is thereby opened, mostly between C atoms 2 and 3 and a new cyclic alc. is formed. In II the end product is an alc. contg. the original ring. The same scheme can be applied to straight-chain amines. Unsaturated hydrocarbons are also mostly formed by loss of  $\text{H}_2\text{O}$ . The hypothesis is strongly supported by the existence of stable nitrites of cyclohexylmethyl-, pinyl-, menthyl and fenchylamines and the frequent occurrence of nitroso compds. of secondary amines in the reaction products. The latter can be most plausibly interpreted as the decompn. products of diazo-amino compds. The assumption of pyrazolines as intermediates was disproved by the fact that pyrazoline forms with  $\text{HNO}_2$ , acrolein and resins. MARY JACOBSEN

**The addition compound of triethylphosphine and carbon disulfide.** J. P. WIBAUT. *Rec. trav. chim.* 44, 239-40(1925).—In a study of the reaction of S with C, W had occasion to identify small quantities of  $\text{CS}_2$  by means of the addn. compd.  $\text{Et}_3\text{PCs}_2$  (I) which Hofmann (*Ann. Suppl.* 1, 26(1861)) stated m. 95°. Hantzsch and Hihbert (*C. A.* 1, 1932) studied it but did not mention the m. p. W has prepd. I in the pure state by adding  $\text{Et}_3\text{P}$  in  $\text{Et}_2\text{O}$  to  $\text{CS}_2$  in  $\text{Et}_2\text{O}$ ; it sepds. as minute crystals, m. 121-2° (decompn.), or 118-9° after sintering. The analysis and crystallographic measurements of H. were confirmed. The m. p. of I as given by H. is wrong. E. J. W.

**Qualitative color test for the Grignard reagent.** HENRY GILMAN AND F. SCHULZE. *J. Am. Chem. Soc.* 47, 2002-5(1925).—The soln. to be tested (0.5 cc.) is treated, at room temp., with an equal vol. of a 1% soln. of Michler's ketone in dry  $\text{C}_6\text{H}_6$ . The reaction product is then hydrolyzed by the slow addn. of 1 cc. of  $\text{H}_2\text{O}$ ; the subsequent addn. of several drops of 0.2% I in AcOH develops a characteristic greenish blue color when Grignard reagent is present. The test color is only shown by those organomagnesium halides having the  $\text{MgX}$  group attached to C. It is also given by  $\text{PhCaI}$ ,  $\text{PhBaI}$ ,  $\text{EtNa}$  and  $p\text{-MeC}_6\text{H}_4\text{Na}$ . A positive test was obtained with 0.037 *M*  $\text{EtMgBr}$  in  $\text{Et}_2\text{O}$ , which is probably the max. for the sensitivity of the test. Unchanged Mg gives a deep blue or purple color slowly, and the soln. should be filtered before applying the test. C. J. WEST

**Germanium. XII. Tetraalkyl and tetraaryl compounds of germanium.** Germanium tetraethoxyl. D. L. TABERN, W. R. ORNDORFF AND L. M. DENNIS. *J. Am. Chem. Soc.* 47, 2039-44(1925); cf. *C. A.* 19, 2429.—*Ge tetraphenyl*, m. 226°, may be prepd. from  $\text{GeCl}_4$  and  $\text{PhMgBr}$  or from  $\text{GeCl}_4$ ,  $\text{PhBr}$  and Na in  $\text{Et}_2\text{O}$ . Crystallographic data are given. *Ge tetra-p-tolyl*, m. 224°, decomp. somewhat at its b. p.; crystallographic data. The *tetra-Pr deriv.*,  $b_{10}$  225°, m. -73°,  $d_{20}^{25}$  0.9539,  $n$  1.451, 1.443, 1.440, 1.433 at 17.5°, 30°, 45° and 61°. It dissolves I but does not appreciably react with it at 50°. The *tetra-isoamyl deriv.*,  $b_{10}$  163-4°,  $d_{20}^{25}$  0.9147,  $n$  1.457, 1.451, 1.444 and 1.438 at 17.5°, 30°, 45° and 61°.  $\text{EtONa}$  and  $\text{GeCl}_4$  gives the hygroscopic *tetra-ethoxy deriv.*, b. 185-7°, m. -81°. The *tetra-Et deriv.* may also be obtained from  $\text{GeCl}_4$  and  $\text{EtMgBr}$ ; it b. 162.5-3°,  $n$  1.443, 1.438, 1.430 and 1.422 at 17.5°, 30°, 45° and 61°. The synthesis of  $\text{SnPh}_4$  by the Fittig reaction also is reported. C. J. W.

**The development of the formalin industry.** OSCAR LOEW. *Z. angew. Chem.* 37, 825-6(1924).—A brief, historical discussion of the industry, particularly of L.'s connection with it, and a description of the hexose (formose) obtainable from  $\text{H}_2\text{CO}$  by condensation in the presence of bases. WM. B. PLUMMER

**Reduction of acetic acid and its derivatives.** G. POVARNIN AND KAL'E. *J. Russ. Phys.-Chem. Soc.* 55, 369-74(1924).—Reduction of  $\text{AcOH}$  to  $\text{AcH}$  by passing a mixt. of its vapors with H over a Pt catalyst and by subjecting it to a spark discharge produced only 0.3% of the theoretical amount. Combination of the 2 methods did not

appreciably alter the results. Ni as the catalyst did not cause the formation of AcH. Electrolysis by means of a weak current of a mixt. of AcONa and  $\text{HCO}_2\text{Na}$  produced chiefly  $\text{HCHO}$ . The amount of CHO group formed rose with the pressure.

W. M. STERNBERG

The perfume group. I. Condensation capacity of isobutyraldehyde. H. THOMS AND H. KAJRE. *Arch. Pharm.* 263, 241-52 (1925).—The investigations here reported were made for the purpose of observing the changes in the character of certain perfumes, as also to prep. products useful as drugs, dyestuffs or disinfectants. In expts. leading to the acetalization of iso-PrCHO with the appropriate alc. by the action of dry gaseous HCl, the following new compds. were obtained in the form of colorless liquids of fusel oil-like odor: *isobutyraldehyde di-isobutylacetal*,  $\text{Me}_2\text{CHCH}(\text{OCH}_2\text{CHMe})_2$ ,  $b_p$  94-5°; *di-isobutylacetal*,  $b_p$  125-7°; *dibenzylacetal*,  $b_p$  194°. By the action of 10% NaOH condensation was effected between iso-PrCHO and ketones to unsatd. derivs. Among the new ketones obtained were *2-methyl-3-hepten-5-one* (I), an isomer of natural methylheptenone, and 3 isomers of thujaketone. I,  $b_p$  167° and has a pleasant ester-like odor,  $d_4$  0.8350,  $n_D$  1.43303. The *semicarbazone*,  $\text{C}_9\text{H}_{17}\text{ON}_2$ , m. 174-5°. On catalytic reduction is formed *2-methylheptanone*,  $b_p$  160-3°,  $d_4$  0.8304,  $n_D$  1.42087 (*semicarbazone*,  $\text{C}_9\text{H}_{17}\text{ON}_2$ , m. 131-2°, which is not depressed when mixed with a semicarbazone, m. 131° prepd. from an iso-AmCOEt, b. 157-65°, obtained by treating iso-AmCOCl with EtLi Grignard). *2-Methyl-3-octen-5-one*,  $b_p$  73-7°,  $d_4$  0.8628,  $n_D$  1.44533 (*semicarbazone*,  $\text{C}_{10}\text{H}_{19}\text{ON}_2$ , m. 147-8°), which on hydrogenation with a Ni catalyst at 210° yields *2-methyl-6-octanone* (*isohexyl Et ketone*), b. 180-5°,  $d_4$  0.8353,  $n_D$  1.43479 (*semicarbazone*,  $\text{C}_{11}\text{H}_{21}\text{ON}_2$ , m. 129°). Treated with boiling alc. and Na, the octenone yields *isohexyl ethylcarbinol*,  $b_p$  74-9°,  $d_4$  0.8102,  $n_D$  1.43850, unaffected by  $\text{NH}_3$  at 110°. *2-Methyl-3-octen-5-one*,  $b_p$  68-78°,  $d_4$  0.9011,  $n_D$  1.47477 (*semicarbazone*,  $\text{C}_{11}\text{H}_{21}\text{ON}_2$ , m. 157-8°), yields with boiling alc. and Na *isooctylpropylcarbinol*,  $b_p$  79-84°. *2,6-Dimethyl-3-hepten-5-one*,  $b_p$  68-74°,  $d_4$  0.8788,  $n_D$  1.45138, yields on reduction *isooctylpropylcarbinol*, b. 173-8°. *Isobutylidenecetophenone*, m. 137.5°. *Isobutylidene-p-aminoacetophenone*, and its HCl salt were prepd. but not pure enough for analysis. The latter on diazotizing and coupling with PhNMe<sub>2</sub> yielded *p-isobutylidenecetodimethylaminoacetobenzene*, likewise in impure condition. *Isobutylidenedurethan*,  $\text{Me}_2\text{CHCH}(\text{NHCO}_2\text{Et})_2$ , m. 157°. II. New derivatives of eugenol. H. THOMS AND MARTHA KEMP. *Ibid* 253-63.—The product of the action of  $\text{HNO}_3$  on dihydromethyleugenol is not a nitroso but a nitro deriv. identical with that already described by Thoms and Zernik (cf *Arch. Pharm. Inst. Univ. Berlin* 1, 10 (1904)). Its  $\text{NH}_2$  deriv. yielded ureas of no pronounced taste. Direct addn. products resulted from the condensation of certain primary aromatic amines with aminodihydromethyleugenol, the OH thereby formed showing great stability and no tendency to split off the elements of  $\text{H}_2\text{O}$ . The following compds. are described: *2,4,5-Propyldimethoxyphenylurea*,  $\text{Pr}(\text{MeO})_2\text{C}_6\text{H}_3\text{NHCO}_2\text{NH}_2$ , m. 200-1°; *2,4,5-Propyldimethoxyphenylthiourea*, m. 193°; *allyl-2,4,5-propyldimethoxyphenylthiourea*,  $\text{Pr}(\text{MeO})_2\text{C}_6\text{H}_3\text{NHCSNHCH}_2\text{CH}_2\text{CH}_3$ , m. 154°. Aminodihydromethyleugenol derivs.: *benzaldehyde*,  $\text{PhCH}(\text{OH})\text{NH}_2\text{C}_6\text{H}_4(\text{OMe})_2\text{Pr}$ , bright yellowish green, m. 79-80° (*HCl salt*, m. 187-9°), yielding with  $\text{ZnCl}_2$  *benzylidene*, m. 85° (*HCl salt*, m. 206°), *anhydromethyleneprotocatechuylaldehyde*,  $\text{CH}_2\text{O}_2\text{C}_6\text{H}_3\text{CH}_2\text{N}(\text{OMe})_2\text{Pr}$ , yellow, m. 112° (*HCl salt*, yellow, m. 197-5°); *o-hydroxybenzylidene*, bright yellow, m. 118-9° (*HCl salt*, m. 101°); *p-methoxybenzylidene*, brilliant yellowish green, m. 68-9° (*HCl salt*, yellow, m. 135°); *cinnamaldehyde*, bright green, decomps. in a desiccator (*HCl salt*, yellow, m. 198° (decomps.)); *cinnamylidene*, red, m. 118° and dyes silk intensely yellow (*HCl salt*, m. 58-9°); *p-dimethylaminocinnamaldehyde*, brown-red, m. 39-40° (*HCl salt*, m. 201-2°, dyes silk, wool and cotton rose to dark red). New high-molecular asymmetrical tertiary alcohols. H. THOMS AND BELA AMBRUS. *Ibid* 263-73.—These alcs. were prepd. for conversion into unsatd. hydrocarbons and a study of the manner of their dehydration. Starting with Me nonyl ketone, the following alcs. were isolated *via* Grignard:  $\text{EtMeC}(\text{OH})\text{C}_9\text{H}_{19}$ ,  $\text{PrMeC}(\text{OH})\text{C}_9\text{H}_{19}$ ,  $\text{iso-PrMeC}(\text{OH})\text{C}_9\text{H}_{19}$ ,  $\text{iso-BuMeC}(\text{OH})\text{C}_9\text{H}_{19}$ ,  $\text{PhMeC}(\text{OH})\text{C}_9\text{H}_{19}$ , all of which are colorless or slightly yellow liquids, and, while asym., are optically inactive, an indication of racemic mixts. For dehydration  $\text{Ac}_2\text{O}$  or 60%  $\text{H}_2\text{SO}_4$  was employed. Their structure was detd. by oxidation and recognition of the resulting acids. The  $\text{H}_2\text{O}$  cleavage involved in general, in addn. to the OH, the H of the largest alkyl group. In the case of methylbenzyl nonylcarbinol, however, the H of the benzyl group was affected. *Methylbenzyl nonylcarbinol*, spicy smelling,  $b_p$  126-9°,  $b_p$  131-3°,  $d_4$  0.8423, yields with  $\text{Ac}_2\text{O}$  at 140-50° *3-methyldodecene*,  $\text{EtMeC} \text{C}_9\text{H}_{19}$ ,  $b_p$  105-7°,  $d_4$  0.7802. *Methylpropyl nonylcarbinol*, spicy liquid,  $b_p$  140-2°,  $b_p$  145°,  $d_4$  0.8406; on heating with  $\text{Ac}_2\text{O}$  and

$ZnCl_2$  it yields 4-methyltridecene,  $C_{15}H_{30}$ , spicy liquid  $b_p$  115–7°, d. 0.788. Methylisopropylphenylcarbinol,  $b_p$  140–2°, d. 0.845; heated with 60%  $H_2SO_4$  at 130–40° it gives the hydrocarbon 2,3-dimethyldodecene,  $Me_2CHCH(Me)C_8H_{18}$ ,  $b_p$  116–22°, d. 0.7858. Methylisobutylphenylcarbinol,  $b_p$  145–50°, d. 0.8386, yields 2,4-dimethyltridecene,  $Me-CHCH_2C(Me):C_8H_{18}$ . Methylphenylphenylcarbinol, impure, converted directly into 2-phenylundecene,  $MeCPh:C_8H_{18}$ ,  $b_p$  166–70°, has the odor of cress (*Tropaeolum maris*). Methylbenzylphenylcarbinol,  $C_{15}H_{20}O$ ,  $b_p$  200–3°, d. 0.9217, smells, like the foregoing, of cress, and yields 2-benzylideneundecene,  $PhCH:C(Me)C_8H_{18}$ ,  $b_p$  180°, d. 0.8790, has an odor of cress. W. O. E.

Beckmann rearrangement. XIV. Distillation of the sodium salts of oximes under reduced pressure. SHIGERU KOMATSU AND TEIKICHI HIRADZUMI. *Mem. Coll. Sci. Kyoto Imp. Univ.* 8A, 273–81 (1925).—The Na salt of  $Ph_2C:NOH$ , distd. at 12 mm., gives 75.5%  $PhCN$  and 23.3%  $NH_3$ .  $PhMeC:NOH$  gave 14.9%  $PhCN$ , 37.3%  $BzOH$  and 47.8%  $NH_3$ , and some  $PhCOMe$ ,  $PhMeC:NOH$ , and a N-contg. compd., m. 186–90°. The Na salt of camphor oxime gave 96% nitrile and 4% acid.  $\alpha-PhCH:NOH$  gave 4.6%  $BzNH_2$ , 81%  $PhCN$ , 7%  $BzOH$  and 7.4%  $NH_3$ , and probably some  $PhC(NH)NH_2$ , m. 78–80°.  $Me_2CHCH_2CH:NOH$  gave 97% nitrile and 3%  $NH_3$ .  $BzNHNa$  gave 84.6% nitrile and 15.38%  $NH_3$ . Thus in the case of the aromatic oximes, the Na salts give the same products as those obtained from the oxime and reduced Cu. It is probable that the first reaction is  $RR'C:NOH \rightarrow RC(NH)ONa + R'$ , the  $RC(NH)ONa$  then gives  $RCN$ .

C. J. WEST

General synthesis of  $\alpha$ -unsaturated acids from malonic acid. I. SIKHIBRUSHAN DUTT. *Quart. J. Chem. Soc.* 1, 297–301 (1925).— $CH_2(CO_2H)_2$  easily condenses with aldehydes in the presence of  $C_6H_5N$  in  $C_6H_5N$  soln. to alkylidene- and arylidenemalonic acids, which, under the influence of  $C_6H_5N$ , particularly on heating, lose  $CO_2$ , giving  $\alpha$ -unsatd.  $CO_2H$  acids in excellent yields.  $AcH$  gives 75% of crotonic acid; 10 g glyoxylic acid gives 1.8 g. fumaric and 2.8 g. maleic acids;  $BzH$  gives 90% of cinnamic acid;  $p-MeC_6H_4CHO$  gives 87%  $p$ -methylcinnamic acid, furfural gives 70% furfuralacrylic acid;  $o-O_2NC_6H_4CHO$  gives 73%  $o$ -nitrocinnamic acid; the  $p$ - and  $m$ -derivs. result in 82% and 90%, resp., piperonal gives 76% piperonylacrylic acid;  $p-MeOC_6H_4CHO$  gives 80%  $p$ -methoxycinnamic acid,  $p-Me_2NC_6H_4CHO$  gives 65%  $p$ -dimethylaminocinnamic acid;  $m-BrC_6H_4CHO$  gives 83%  $m$ -bromocinnamic acid,  $o-HOC_6H_4CHO$  gives 20%  $o$ -coumaric acid; carbethoxyvanillin gives 12% of ferulic acid; dicarbethoxyprotocatechualdehyde gives 7% caffeic acid;  $PhCH:CHCHO$  (heating the reaction mixt. 2 hrs.) gives 70% of cinnamylidenemalonic acid; on longer heating 60% of the cinnamylidenemalonic acid.  $Me_2CO$  gives 60% of  $\beta,\beta$ -dimethylacrylic acid;  $Et_2CO$  gives 35% of  $\beta,\beta$ -diethylacrylic acid; cyclohexanone gives not over 5% of cyclohexylidenemalonic acid.

C. J. WEST

The index of refraction of china wood oil and the composition of  $\alpha$ - and  $\beta$ -eleostearic acids. J. BÖESEKEN AND MISS H. J. RAVENSWAAY. *Rec. trav. chim.* 44, 241–3 (1925).—China wood oil (I), is about 90% glyceride of  $\alpha$ -eleostearic (or  $\alpha$ -eleomargaric) acid (II), considered to be an isomer of linolic acid because its I no. (160–70) indicates 2 double bonds. II, m. 47°, can be converted into the  $\beta$ -isomer (III), m. 67°. I irradiated with a Hg lamp is converted in 48 hrs. into a solid mass of the glyceride of III, m. 58.5°. The mol. refraction of purified I is 284.6 (calcd. 267.6); for III it is 289.9 (calcd. 267). On the basis of these data and a comparison with unsatd. hydrocarbons B. and R. conclude that I and III are probably isomeric compds. with 3 double bonds. The mol. refraction of pure II is 93.05 (calcd. 86.04); of linolic acid 86.57 (calcd. 86.04). I hydrogenated in the presence of  $Ni$  absorbed 7.9 mols.  $H_2$  (calcd. 9.0). The results indicate that there are more than 2 double bonds but B. and R. are unable to state why the calcd. amt. of  $H_2$  was not absorbed. II is therefore not a linolic acid but is a linoleic acid and both the  $\alpha$ - and  $\beta$ -forms have the compn.  $Me(CH_2)_7CH:CHCH_2CHCH:CHCH_2CO_2H$ . This result seems to disagree with the I no. but it is pointed out that compds. with 3 conjugated bonds unite easily with only 2 mols. of  $Br_2$ .

E. J. WITZEMANN

The composition of  $\alpha$ -eleostearic acid of Chinese wood oil and its isomer  $\beta$ -eleostearic acid. J. BÖESEKEN AND H. J. RAVENSWAAY. *Verslag. Akad. Wetenschappen Amsterdam* 34, 204–7 (1925).—The very high mol. refractions of  $\alpha$ - and  $\beta$ -eleostearic acids and their derivs., which exceeds by 5–7 that calcd. with the aid of the generally accepted formula, suggested the existence of 3 conjugated double bonds. The absorption of 2.65 mols.  $H$  by wood oil and  $Et \alpha$ -eleostearate on hydrogenation with  $H$  and  $Ni$  catalyst confirmed this hypothesis. The formula suggested by B.,  $Me(CH_2)_7CH:CHCH:CHCH:CHCH_2CO_2H$ , is in keeping with the high drying power and the

formation of large quantities of azelaic and valeric acids by ozonization, but does not explain the formation of succinic acid. The low I value, corresponding to 2 double bonds only may be attributed to the abnormal behavior of compds. with 3 conjugated double bonds as was recently stated by Mueller.

MARY JACOBSEN

**Leprosy. XXXVII. Fractionation of chaulmoogra oil. II. Evidence of the existence of a highly unsaturated optically active acid.** RICHARD WRENSHALL AND A. L. DEAN. *U. S. Public Health Service Bull.* 141, 12-23 (1924); cf. *C. A.* 15, 728.—Repeated fractionation of the liquid acid residue of chaulmoogra acids and the application of the Pb salt-ether method to the highly unsatd. fraction yielded an acid of the I no 1683 (Hübl), which rose to 1504 after a longer period. Its  $d_{20}^{25}$  was 0.9322,  $n_D^{25}$  1.4735,  $\alpha_D^{25}$  53.1°, acid no. 201.2. Since the catalytic hydrogenation led to dihydrochaulmoogric acid, the new acid is very probably  $C_{17}H_{21}CO_2H$ , a chaulmoogric acid with another double bond. Palmitic acid was recovered from the impure fractions of the reduction product. **XXXVIII. Catalytic reduction of chaulmoogric and hydnoecarpic acids.** A. L. DEAN, RICHARD WRENSHALL AND G. FUJIMOTO, *Ibid.* 24-7; cf. *J. Chem. Soc.* 85, 838, 851 (1904); *C. A.* 1, 1561, 2144.—The great difference between the structure of chaulmoogra oil acids and other fatty acids suggests that their mol. asymmetry or the ethylene linkage or both are possibly responsible for the therapeutic effect. Hydrogenated acids were prepd. for the purpose of testing their physiol. action. Dihydrochaulmoogric acid, m. 71-71.5°, I no. 0.76-0.83,  $\alpha_D^{25}$  (5%  $CHCl_3$  soln.) -0.12 to +0.57°, acid no. 199.8, m. p. of Et ester 16.5°, was obtained in nearly theoretical yield by 48 hrs. reduction of a 17% purified chaulmoogric acid soln. in 95% alc. by H in presence of colloidal Pt-Pd. More catalyst must be added after 16-24 hrs. Esterification occurs at the same time and slows down hydrogenation. The 5%  $H_2O$  retards esterification without giving rise to emulsions. Dihydrohydnoecarpic acid,  $C_{17}H_{21}CO_2H$ , m. 63°, optically inactive, was obtained in the same way. M. J.

**Condensation of nitriles with thioamides. IV. Thioamides with phenylimino chlorides.** SEIICHI ISHIKAWA. *Sci. Papers Inst. Phys. Chem. Res. (Tokyo)* 2, 229-304 (1925); cf. *C. A.* 18, 234, 1468.— $MeC(SH):NH$  and  $MeC(NPh)Cl$  in Et-O gave 72% of  $MeC(NPh)SH$ ;  $PhC(SH):NH$  gave 46%  $MeC(NPh)SH$ .  $MeC(SH):NH$  and  $PhC(NPh)Cl$  gave 94%  $PhC(NPh)SH$ .  $PhC(SH):NH$  and  $PhC(NPh)Cl$  gave 50% of the theoretical amt. of  $PhCN$  and 96% of the theory of  $PhC(NPh)SH$ .

C. J. WEST

**Relations between rotatory power and structure in the sugar group. X. C. S. HUDSON AND ALFRED KENZ.** *J. Am. Chem. Soc.* 47, 2052-5 (1925); cf. *C. A.* 19, 1230.—The prepn. of  $\alpha$ -Cl, -Br and -I derivs. of acetylactose is described. The  $\alpha$ -Cl deriv., m. 120-1° and has  $[\alpha]_D^{25}$  83.9° in dil.  $CHCl_3$ ,  $[\alpha]_D^{25}$  63.2° (0.4823 g. in 50 cc. of soln. in  $C_6H_6$ ); in 1 case a small amt. of compd. (Cl deriv. of lactose octaacetate?), m. 160°,  $[\alpha]_D^{25}$  71.7° ( $CHCl_3$ ), was obtained.  $\alpha$ -Br deriv., m. 145° (decompn.),  $[\alpha]_D^{25}$  108.7° (1.0118 g. in 100 cc. of soln. in  $CHCl_3$ ).  $\alpha$ -I deriv., m. 145° (decompn.),  $[\alpha]_D^{25}$  136.9° (0.9475 g. in 100 cc. of soln. in  $CHCl_3$ ). These values agree with the theoretical requirements.

C. J. WEST

**Decomposition of ethyl diazoacetate by copper acetylene.** E. MÜLLER AND C. GOTTFRIED. *J. prakt. Chem.* 110, 40-1 (1925).— $N_2CHCO_2Et$  and  $Cu_2C_2$  in dry  $Et_2O$  liberate nearly the theoretical amt. of N in 10 hrs. and give Et fumarate, b.p. 98-100°. The product was identified by sapon. and analysis of the Ag salt.

C. J. WEST

**The preparation of acyclic  $\delta$ -diketones.** E. E. BLAIR AND M. MONTAGNE. *Compt. rend.* 180, 1345-6 (1925).—The condensation of  $EtMgBr$  with  $(Et_2NOCCH_2)_2CH_2$  yields 20-30% dipropionylpropane (cf. *C. A.* 15, 3619) and an oil (I), b.p. 155-60°. Through the semicarbazones I may be sepd. into diethyl- $\gamma$ -propionylbutylamide,  $EtCO(CH_2)_2CONEt_2$  (II), b.p. 163° (semicarbazone, m. 126-7°), and a ketonic amine,  $EtCO(CH_2)_2CEtNEt_2$  (III), b.p. 161° (semicarbazone, m. 90°; picrate, m. 106-7°). The constitution of these is indicated by the fact that II on hydrolysis, with  $HBr$  gives  $EtNH$ ,  $\gamma$ -propionylbutyric acid, m. 49-50°, and methylidihydroresorcinol; III, boiled with  $Ac_2O$ , yields an ethylenic ketone and  $AcNEt_2$ .

I. P. ROSE

**Simplified method for the preparation of dimethylglyoxime.** W. L. SEMON AND V. RICHARD DAMERELL. *J. Am. Chem. Soc.* 47, 2033-9 (1925).—The yield of biacetyl monoxime (I) is 65% when  $MeEtCO$  contg. 2%  $HCl$  is treated with  $AmNO_2$ ,  $BuNO_2$  or  $EtNO_2$ . With pure  $MeEtCO$  the use of more than 75% of the calcd. amt. of  $EtNO_2$  is without advantage. The most satisfactory condensing agents are  $HCl$  (2.5-3%),  $PbCl_2$  (8%) and  $POCl_3$ . A small quantity of  $H_2O$  has very little effect upon the yield, the effect being much less marked than that of the impurities present in the com.  $MeEtCO$ . I can also be prepd. by the use of  $NOCl$  (51% yield) but its use is unsatisfactory on a

large scale. I is best isolated by extg. with NaOH, acidifying with AcOH and distg. *in vacuo*. When dimethylglyoxime (II) is the final product, it is not necessary to isolate the I, for when the aq. distillate contg. the I is allowed to stand for several hrs. with a slight excess of Na hydroxylaminemonesulfate, pure cryst. II is deposited. 1 (620 g.) gives 575 g. II.

C. J. WEST

Thermochemical studies on the oximes. III. Stereoisomeric dioximes. A. DORABIALSKA. *Roczniki Chem* 4, 265-86(1924); cf. C. A. 17, 1458; 18, 1279.—The heats of formation of the Na salts of glyoxime and methylglyoxime suggest the possibility of stereoisomerization, 3 stereoisomeric forms being distinguished for glyoxime and 4 for methylglyoxime. In H<sub>2</sub>O each of these 2 oximes forms a mixt. of stereoisomerides. Electronic formulas are suggested for the stereoisomeric oximes.

B. C. A.

Supposed dimeric anils of alkylated glutaric acids. K. v. AUWERS. *Ann* 443, 310-4(1925); cf. *Ann.* 285, 226(1895).—The compds. previously reported as dimeric anils are actually dianilides (private communication by Windaus)  $\alpha$ -Methylglutaric acid dianilide, m. 175°; di-*p*-tolide, m. 174-5°; di- $\beta$ -naphthide, m. 227-8° (the compd. m. 166-9° is a mixt.)  $\alpha$ , $\alpha$ -Dimethylglutaric acid di-*p*-tolide, m. 237°;  $\alpha$ -naphthid., m. 204-5°; di- $\alpha$ -naphthide, m. 245-6°;  $\beta$ -naphthid., m. 168-9°; di- $\beta$ -naphthide, m. 232°.  $\alpha$ , $\alpha$ -Diethylglutaric acid di-*p*-tolide, m. 224-5°.

C. J. WEST

Derivatives of citraconic acid. I. Synthesis of methyltartaric acid and the decomposition of dihydroxymaleic acid. W. F. GORREL. *J. Am. Chem. Soc.* 47, 1990-8 (1925).—The addn. of HOCl to Na citraconate (4% aq. soln.) gives 45-50% of the Cl deriv. All the expts. attempting to hydrolyze the acid or its Ba salt directly to methyltartaric acid (I) indicated that any attempt in this direction is practically futile. The Ba salt, with 10% excess of 3% Ba(OH)<sub>2</sub> at 35°, gives quant. Ba hydroxycitraconate. Hydrolysis of 200 g. of this salt with H<sub>2</sub>SO<sub>4</sub> under controlled conditions gave 65 g. I, m. 100° (decompn.). Oxidation of I with H<sub>2</sub>O<sub>2</sub> gave a soln. which may contain hydroxyethylketosuccinic acid, but the acid was too unstable to be isolated; PhNHNH<sub>2</sub> gave lactaldehyde osazone; Ba(OH)<sub>2</sub> gave diketobutyric acid. The possible mechanism of the reactions is discussed.

C. J. WEST

Stereochemistry of the tetrahedral carbon atom. I. Novel inversion phenomena. RICHARD KUHN and FRIEDRICH EBEL. *Ber.* 58B, 910-32(1925).—As stated by Lossen (*Ann.* 348, 273(1906)), addn. of HOCl to maleic acid gives only 1 chloromaleic acid (I), m. 145° (m. ps. are cor. unless otherwise stated), which in alkalis loses HCl and is quant. converted into fumarylglycidic acid; this can be resolved by means of morphine in alc. into optical antipodes and is therefore *trans*-ethyleneoxidedicarboxylic acid (II). Contrary to L. and to Dakin (C. A. 16, 211), however, addn. of HOCl to fumaric acid does not give a homogeneous product; the mother liquors from the Ba salt of II contain the 2nd chloromaleic acid (III), which on energetic treatment with alkalis gives *cis*-ethylene oxide-1,2-dicarboxylic acid (IV), m. 149°; this m. 60° lower than II and, unlike the latter, is readily sol. in Et<sub>2</sub>O. All attempts to prep. an anhydride from it have failed. On addn. of HCl and HBr it gives III, m. 153.5°, and a bromomaleic acid (V), m. 136°, resp. V has the same m. p. as its isomer (VI) (Lossen). The velocity with which these halomaleic acids lose halogen acid with alkalis differs extraordinarily. Thus, in 0.5% solns with 4 equivs. NaOH at 0°, 0.5 of the halogen acid is liberated from VI, I, V and III in 0.5, 18, 600 and about 200,000 min., resp. The difference in the firmness with which the HX is held has been made the basis of a method for analyzing the halomaleic acids in the presence of each other. On boiling II in H<sub>2</sub>O it gives 37% *dl*- (VII) and 63% *meso*-tartaric acid (VIII), while IV both in H<sub>2</sub>O and in alkalis yields VII exclusively. On the other hand, I heated in H<sub>2</sub>O gives a mixt. of VII and VIII while III gives VIII alone. K. and E. believe their conversion of IV into VII is the 1st unimpeachable proof of the quant. *trans*-cleavage of a ring system. Fischer's formulas for the sugars are based on reactions which, as is now known, involve the opening of an O ring (reduction, oxidation, osazone formation, etc.) and in view of the evidence offered in this paper of the possibility of *trans*-cleavage of a ring, it does not necessarily follow that when the O bridge in a sugar is broken the newly formed HO group takes a position on the same side of the formula as that originally occupied by the bridge. These observations also invalidate the generality of Meisenheimer's rule that "in the cleavage of a ring there can result only a structure which contains the 2 fragments adjacent to each other" (C. A. 16, 2105). Geometrically, IV corresponds to VIII and it might be assumed that the formation of VII from IV is the result of a secondary rearrangement of VIII produced primarily, although preformed VIII cannot be transformed into VII under the conditions of the expt. Such reactions, *i. e.*, reactions in which the assumed unstable intermediate product cannot be shown experimentally to change into the final product under the same external conditions, are designated secondary transformations of the 1st kind,

while those in which the assumed intermediate product can, under the same exptl. conditions, be converted into the final product are called secondary transformations of the 2nd kind. It follows directly that the results of stability detns. can be only of limited value in establishing configurations. *d*-II, m. 209°, is obtained in 27% yield from fumaric acid, the mother liquors from its Ba salt on further treatment with NaOH yield almost an equal amt. of IV, which can be recrystd. unchanged from boiling AcCl and  $\text{Ac}_2\text{O}$ , *mono-K* salt, long crystals with 1  $\text{H}_2\text{O}$ ; the *Ca* and *Ba* salts cryst. with 2  $\text{H}_2\text{O}$ ; *Ag* salt, sensitive to light. *Morphine* salt of *d*-II, m. 180° (decompn.),  $[\alpha]_D^{20} -76.8^\circ$ ; *di-NH<sub>4</sub>* salt,  $[\alpha]_D^{20} 50.1^\circ$  (calcd. for the free acid); free *d*-II, m. 180° (decompn.),  $[\alpha]_D^{18} 100^\circ$  ( $\text{H}_2\text{O}$ ). The *l*-II (prepd. from *d*-tartaric acid), m. 180° (decompn.),  $[\alpha]_D^{18} -100^\circ$ . Attempts to resolve IV with alkaloids failed; the primary *morphine* salt, m. 180° (uncor.) with decompn.,  $[\alpha]_D^{20} -80.8^\circ$ . C. A. R.

The thermal decomposition of derivatives of oxalacetic esters—a unimolecular reaction. D. L. WATSON *Proc. Roy. Soc. (London)* 108A, 132-53 (1925).—Ethoxyoxalacetic, oxalpropionic and oxalsuccinic esters decomp. thermally at temps. between 140° and 200° according to the unimol. law. The reaction is unaffected by the solvents  $\text{C}_6\text{H}_5\text{Br}$ ,  $\alpha$ - and  $\beta$ - $\text{C}_6\text{H}_5\text{OMe}$ , HCl gas or moisture, but is retarded by an excess of CO. The velocity const. is found to vary with the temp. according to the Arrhenius law,  $k = Ae^{-Q/RT}$  and if *A* is the probability per sec. that an active mol. will decomp. (cf. Christiansen and Kramers, *C. A.* 17, 916, 1935), a relation between *Q* and *A* is expected for similar compds. and W. finds *Q/log A* is const. If a "reaction chain" activation obtains, theoretical considerations lead to the conclusion that the reaction should be autocatalytic. The decompn. of phenyloxalacetic ester is found to be autocatalytic. No evidence is found to support the Lewis-Perrin radiation theory, either from absorption spectra, illumination or theory. D. S. VILLARS

Halogenation. XII. Derivatives of carbamic esters. Chlorine as a simultaneous oxidizing and chlorinating agent. II. RASIK LAL DATTA and BIRHU CHARAN CHATTERJEE. *Quart. J. Indian Chem. Soc.* 1, 311-3 (1925); cf. *C. A.* 17, 1449. —*iso*- $\text{C}_6\text{H}_5\text{CO}_2\text{NH}_2$  in MeOH, treated with Cl<sub>2</sub>, gives *isopropyl methylenedimethylcarbamate*, m. 110°.  $\text{MeCO}_2\text{NH}_2$  in  $\text{PhCH}_2\text{OH}$  with Cl gives *benzylidenedimethylurethan*, m. 175°; *di-Pr* deriv., m. 146.7°; *di-iso-Pr* deriv., m. 148°; *di-iso-Bu* deriv. C. J. WEST

Unsaturated reduction products of the sugars and their derivatives. X. Pseudo-glucal and dihydropseudoglucal. MAX BERGMANN. *Ann.* 443, 223-42 (1925); cf. *C. A.* 19, 1409. —Triacetylglucal, boiled with 20 parts of  $\text{H}_2\text{O}$  for 15 min. and the sirupy residue (largely diacetylpsudoglucal) boiled with  $\text{HCOEt}$ ; in abs. EtOH gives *diacetylpsudoglucal Et cycloacetal*, b<sub>1</sub> 130°, m. 81-2°,  $[\alpha]_D^{20} 102.8^\circ$  ( $\text{C}_6\text{H}_6$ ).  $\text{Ba(OH)}_2$  at 20° gives the free *acetal*, m. 100-1°,  $[\alpha]_D^{20} 100.3^\circ$  (EtOH), 71.26° ( $\text{H}_2\text{O}$ ); the HCl-pine wood reaction is green. Boiling concd. HCl decomposes the acetal. HCl,  $\text{m-C}_6\text{H}_4(\text{OH})_2$  and AmOH give a pronounced violet to wine red color, which is rather permanent. Short boiling does not reduce Fehling soln. The glucal is very readily hydrolyzed by  $\text{H}_2\text{O}$  or 0.0001 *N* HCl, the rotation becoming const. in about 20 min. The course of the hydrolysis is shown by curves. Reduction in MeOH with Pd and H gives the  $\alpha$ -*dihydro* deriv. (2,3-bisdesoxyglucose *Et cycloacetal*) (I), m. 72-2.5°,  $[\alpha]_D^{17} 156^\circ$  (abs. EtOH),  $[\alpha]_D^{20} 137.8^\circ$  ( $\text{H}_2\text{O}$ ); *diacetate*, b<sub>1</sub> 125-7°,  $n_D^{20} 1.4457$ ,  $[\alpha]_D^{20} 117.9^\circ$  (EtOH);  $\text{Ba(OH)}_2$  gives the original acetal, but its rotation is slightly higher, 139.5° ( $\text{H}_2\text{O}$ ). Reduction of diacetylglucal gives *dihydropseudoglucal diacetate* (2,3-bisdesoxyglucose *diacetate*) (II), m. 75-6°,  $[\alpha]_D^{20} 42.74^\circ$  ( $\text{H}_2\text{O}$ ), unchanged after several days; boiling Fehling soln. is scarcely reduced;  $\text{PhNHNH}_2$  AcOH gives an oil. In  $\text{CdH}_2\text{N}$ ,  $[\alpha]_D^{20}$  is 116.7°, changing to 77.5° after 12 hrs. *Et cycloacetal*, b<sub>1</sub> 121-3°,  $n_D^{20} 1.4490$ ,  $[\alpha]_D^{20} 47.6^\circ$  (EtOH), this is a mixt. of at least 2 isomers, for sapon. with  $\text{Ba(OH)}_2$  gives I and the  $\beta$ -deriv., m. 95°,  $[\alpha]_D^{20} -29.5^\circ$  ( $\text{H}_2\text{O}$ ), completely hydrolyzed by 0.001 *N* HCl in 8 min. II is further reduced in AcOH by Pd and H to *tetrahydropseudoglucal diacetate*, b<sub>1</sub> 160°,  $n_D^{20} 1.4587$ ,  $[\alpha]_D^{20} 2.2^\circ$  (EtOH), reduces only traces of Fehling soln. on long boiling. II and satd. MeOH-NH<sub>3</sub> give *bis[dihydropseudoglucalyl]mine*, m. 142-3°. C. J. WEST

"Glucose" or "Glucose"? G. BRUNNA *Z. angew. Chem.* 38, 351 (1925).—To avoid the irregular and sometimes misleading use of the above words in French and English, B. advocates adherence to the older form "invert sugar" to denote the mixt. of dextrose and levulose commonly known as glucose. WM. B. PLUMMER

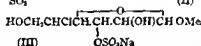
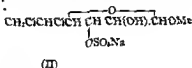
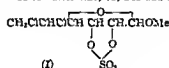
Replacement of reactive hydrogen atoms in sugars, hydroxy and amino acids by

the triphenylmethyl residue. BURCKHARDT HELFERICH, LUDWIG MOOG AND ADOLF JÜNGER. *Ber.* 58B, 872-86 (1925); cf. *C. A.* 19, 230.—The prepn. of  $\text{Ph}_3\text{C}$  ethers has been extended to other sugars besides  $\alpha$ -Me glucoside. The cryst. compd. (I) obtained from *d*-glucose readily yields a *tetra-Ac deriv.* (II) different from that obtained by treating with  $\text{Ac}_2\text{O}$  the original  $\text{C}_6\text{H}_5\text{N}$  soln. of glucose and  $\text{Ph}_3\text{CCl}$  without first isolating the I. Both acetates give acetodibromoglucose with  $\text{PBr}_3$ , whence it is concluded that they are derivs. of 6-triphenylmethyl- $\alpha$ - and  $\beta$ -*d*-glucose, resp., an assumption in harmony with the fact that the cryst. I shows (decreasing) mutarotation. The  $\text{Ph}_3\text{C}$  residue is very sensitive not only to acids but, unlike all other ethers of  $\text{Ph}_3\text{COH}$  hitherto prepd., to alkalis in  $\text{MeOH}$  also. I and the corresponding *galactose deriv.* (III) are sol. in many org. solvents and are readily converted back into the free sugars. A *triphenylmethylmonoacetone-d-glucose* was prepd. and isolated as the *di-Bz deriv.* (IV) (not yet definitely shown to be homogeneous). *Triphenyl-d-glucosic phenylhydrazide* (V) and  $\text{Ph}_3\text{C}$  derivs. of various HO and  $\text{NH}_2$  compds. were likewise obtained. In the prepn. of these ethers there is often formed as by-product a pure white cryst. substance (VI) which is apparently an addn. product of  $\text{Ph}_3\text{COH}$  and  $\text{HCl}$  (or  $\text{Ph}_3\text{CCl}$  and  $\text{H}_2\text{O}$ ). I (30 g., together with 5 g. VI, from 36 g. glucose in 180 cc abs.  $\text{C}_6\text{H}_5\text{N}$  and 58 g.  $\text{Ph}_3\text{CCl}$  kept 1-2 days at room temp.), needles with 2  $\text{EtOH}$ , begins to sinter  $45^\circ$ , m.  $57-8^\circ$ ; anhyd., it begins to sinter  $60^\circ$ , softens more and more and finally evolves gas at  $100^\circ$ ,  $[\alpha]_D^{25}$  in  $\text{C}_6\text{H}_5\text{N}$   $59.6^\circ$  (initial),  $38.0^\circ$  (final, after 90 hrs.), reduces hot Fehling soln., hydrolyzed by  $\text{HCl}$  in soln. ( $\text{MeOH}$ ,  $\text{Et}_2\text{O}$ ,  $\text{CHCl}_3$ ) or by 0.5% alc.  $\text{NaOH}$  to glucose and  $\text{Ph}_3\text{COH}$ . III (yield, about 30%), contains 1 mol.  $\text{EtOH}$  when air-dry and loses only 0.5 mol. even after several days under 2 mm. at  $67^\circ$  over  $\text{P}_2\text{O}_5$ , m. (air-dry)  $73-5^\circ$ ,  $[\alpha]_D^{25}$  in  $\text{C}_6\text{H}_5\text{N}$   $0.58^\circ$  (initial),  $2.24^\circ$  (final after 20 hrs.), the dried product begins to sinter  $76^\circ$  and decomps. about  $108^\circ$ . *Tetra Ac deriv.* of I, m.  $129-31^\circ$ ,  $[\alpha]_D^{27}$   $97.8^\circ$ ,  $[\alpha]_D^{22}$   $97.4^\circ$  ( $\text{C}_6\text{H}_5\text{N}$ );  $\beta$ -isomer (yield, about 27%), m.  $163-4^\circ$ ,  $[\alpha]_D^{25}$   $44.8^\circ$ ,  $[\alpha]_D^{24}$   $45.3^\circ$  ( $\text{C}_6\text{H}_5\text{N}$ ). IV, needles m. sometimes  $78-9^\circ$ , sometimes  $97-9^\circ$ ,  $[\alpha]_D^{21}$  in  $\text{C}_6\text{H}_5\text{N}$   $-4.5^\circ$  and  $-4.0^\circ$ , resp., reduces Fehling soln. only after hydrolysis with acids. V (yield, about 65%), leaflets with 2.5  $\text{H}_2\text{O}$ , sinters about  $93^\circ$ , decomps.  $101^\circ$ ,  $[\alpha]_D^{25}$  in  $\text{C}_6\text{H}_5\text{N}$   $3.0^\circ$  (air-dry),  $4.8^\circ$  (anhyd.) hydrolyzed by 1%  $\text{HCl}$  in  $\text{MeOH}$  in 20 hrs. at room temp. and by boiling 5% alc.  $\text{KOH}$  in 30 min. to the *K salt* (yield, 71%), decomps.  $198-9^\circ$ ,  $[\alpha]_D^{24}$   $7.7^\circ$  ( $\text{Me}_2\text{CO}$ ). *Tetra-Bz deriv.* of V (yield, 80%), sinters  $168^\circ$ , m.  $173^\circ$ ,  $[\alpha]_D^{18}$   $36.2^\circ$  ( $\text{C}_6\text{H}_5\text{N}$ ), rapidly loses the  $\text{Ph}_3\text{C}$  residue in  $\text{MeOH}$  or  $\text{CHCl}_3$  contg.  $\text{HCl}$ . *p-Hydroxybenzoic anhydride mono-triphenylmethyl ether* (?),  $\text{C}_{21}\text{H}_{15}\text{O}_4$  (0.6 g. from 2 g. *p*- $\text{HOC}_6\text{H}_4\text{CO}_2\text{H}$  and 4 g.  $\text{Ph}_3\text{CCl}$  in boiling  $\text{C}_6\text{H}_5\text{N}$ ), m.  $219-20^\circ$ , mol. wt. in boiling  $(\text{CH}_3\text{Br})_2$  484-8. *Et*  $\beta$ -triphenylmethoxypropionate (yield, 48%), m.  $104-5^\circ$ ; 1%  $\text{HCl}$  in  $\text{MeOH}$  hydrolyzes both the ether and ester, alc.  $\text{KOH}$  only the ester grouping, giving 90% of the free acid, m.  $163-4^\circ$ , whose *Na salt* m.  $258-9^\circ$ .  $\text{PhOCPh}_3$  (yield, 28%), m.  $103^\circ$ . *Triphenylcarbinol-HCl* (VI), best obtained from  $\text{Ph}_3\text{CCl}$  in  $\text{C}_6\text{H}_5\text{N}$  with 1 mol.  $\text{H}_2\text{O}$ , m.  $174^\circ$ , smoothly yields  $\text{Ph}_3\text{COEt}$  on recrystn. from  $\text{EtOH}$  and in the air gradually decomps. into  $\text{Ph}_3\text{COH}$  and  $\text{HCl}$ . *Bis(triphenylmethyl)urea* (2.8 g. from 0.5 g. urea and 4.7 g.  $\text{Ph}_3\text{CCl}$  in  $\text{C}_6\text{H}_5\text{N}$  on the  $\text{H}_2\text{O}$  bath), needles with 2  $\text{EtOH}$ , m.  $245^\circ$ , unchanged by 3 hrs. boiling with 10% alc.  $\text{KOH}$  but hydrolyzed by boiling 0.5 hr. with 2%  $\text{HCl}$  in  $\text{MeOH}$ . *Triphenylmethylthiourea*, from equiv. amts. of  $\text{Ph}_3\text{CCl}$  and  $\text{CS}(\text{NH}_2)_2$  in hot  $\text{C}_6\text{H}_5\text{N}$ , m.  $222^\circ$  (decompn.). *Et N-triphenylmethylglycolate* (yield, 61%), m.  $114^\circ$ , loses both the ether and ester groups on boiling 1 hr. with 5% alc.  $\text{KOH}$  but 2% alc.  $\text{KOH}$  after 2 days at room temp. yields the free acid (66%), m.  $168^\circ$ , decomps. above  $180^\circ$ , loses the  $\text{Ph}_3\text{C}$  group when boiled 0.5 hr. with 10% alc.  $\text{KOH}$ ; *Na salt*, needles with about 7  $\text{H}_2\text{O}$ , m. below  $100^\circ$ , solidifies and m. again  $265-6^\circ$ ; *Cu salt*, lilac crystals with 3  $\text{MeOH}$ , begins to become pale about  $100^\circ$ , turns green and decomps. about  $159^\circ$ . *Et N-triphenylmethyl-dl-alanine* (yield, 43%), m.  $100^\circ$ ; both the ether and ester groupings are hydrolyzed after 2 hrs. boiling with 5% alc.  $\text{KOH}$  but after 15 min. is obtained the free acid, crystals with 0.5  $\text{EtOH}$ ; *Na salt*, hygroscopic. *Et N-triphenylmethylglycylglycine* (yield, 54%), m.  $161^\circ$ ; free acid (yield, 60%), m.  $180^\circ$ ; *Na salt*, becomes discolored around  $250^\circ$ , does not m.  $300^\circ$ . *N-Triphenylmethylidiphenylamine*, m.  $240^\circ$ , mol. wt. in boiling  $\text{PhMe}$  403-64; the  $\text{Ph}_3\text{C}$  residue cannot be split off with either acids or alkalis; concd.  $\text{H}_2\text{SO}_4$  dissolves it partially and slowly but without hydrolysis.

C. A. R.

A *d*-glucose 5,6-dichlorohydrin. BURCKHARDT HELFERICH, GOTTFRIED SPROCK AND EDUARD BESLER. *Ber.* 58B, 886-91 (1925); cf. *C. A.* 17, 3167.—The present work establishes that  $\alpha$ -methyl-*d*-glucoside dichlorohydrin sulfate has the structure I. Its 1st alk. sapon. product (II) yields on further treatment the salt III. On acid hydrolysis, the products differ with the conditions. Conc.  $\text{H}_2\text{SO}_4$ , at about  $70^\circ$  hydrolyzes off the

OSO<sub>3</sub>H group more rapidly than the MeO residue and yields  $\alpha$ -methyl-*d*-glucoside 5,6-dichlorohydrin (IV). Concd. HCl at room temp attacks practically only the MeO group, giving *d*-glucose 5,6-dichlorohydrin 2,3-sulfate (V), which titrates practically neutral but is converted by alkalis at room temp. almost instantaneously into a monobasic acid (probably by sapon of the ester grouping on C atom 2). On the other hand III (or the NH<sub>4</sub> salt) allowed to stand 2 days with concd. HCl at room temp. or heated 2 hrs at about 70° with 12 *N* H<sub>2</sub>SO<sub>4</sub> yields *d*-glucose 5,6-dichlorohydrin (VI). Since on substitution of a Cl atom on C atom 5 and perhaps also on hydrolysis of the H<sub>2</sub>SO<sub>4</sub> residue Walden inversions may occur at C atoms 2, 3 and 5 it must be left for further study to det. whether the above compds have the same configuration as *d*-glucose at these C atoms. Na  $\alpha$ -methylglucoside 5-chlorohydrin sulfate (III) (0.35 g from 0.6 g II allowed to stand 1 day in 3.9 cc. of 5 *N* NaOH), crystals with 1 H<sub>2</sub>O, m, 131° (foaming) or, anhyd, 135°, reduces Fehling soln. only after hydrolysis with acids, splits off no Cl on short boiling with AgNO<sub>3</sub>,  $[\alpha]_D^{25}$  48.9° (H<sub>2</sub>O). Diacetate of IV, m 110°; dibenzoate, m 117°,  $[\alpha]_D^{25}$  180.60° (C<sub>6</sub>H<sub>5</sub>N); di-*p*-toluenesulfonate, turns gray and sinters around 117° and then does not change further up to 220°,  $[\alpha]_D^{25}$  95.8° (C<sub>6</sub>H<sub>5</sub>N). VI, darkens 168°, m 180°, is not fermented by ordinary brewers' yeast,  $[\alpha]_D^{25}$  in C<sub>6</sub>H<sub>5</sub>N 180.05° after 15 min, 126.1° after 86 hrs, strongly reduces Fehling soln. is also obtained (1.2 g yield) from 5 g I allowed to stand 1 day in 95% MeOH satd. at 0° with NH<sub>3</sub>, then evapd, in *vacuo* to a sirup and allowed to stand 2 days in concd. HCl; phenyllosazone, amorphous; *p*-nitrophenyllosazone. V (3.2 g. from 5 g. I), crystals with 1 H<sub>2</sub>O, m, 104-6° (decompn), reduces hot Fehling soln.,  $[\alpha]_D^{17}$  in H<sub>2</sub>O -66.10°, -45.47°, -11.54°, -11.09° after 0.25, 75, 242 and 292 hrs., resp.



C. A. R.

Structure of benzene. J. J. VAN LAAR. *Chem. Weekblad* 22, 286-7(1925); cf. C. A. 13, 3048; 18, 1991.—Lefy's criticism of Kekulé's benzene model is unfounded. The presence of a double bond to each C atom is proved by the value of  $10\sqrt{a}$  of the equation of state which is 1.55 instead of 3.1 for the C atoms of a no. of benzene homologs, halogen and NH<sub>2</sub> deriva.

MARY JACOBSEN

The synthetic preparation of the homologs of benzyl chloride. M. SOMMELET. *Compt. rend.* 180, 1349-51(1925).—Condensing MeOCH<sub>2</sub>Cl with PhMe in the presence of SnCl<sub>4</sub> yields chloromethyltoluene (I), and a residue of 2 fractions, II, b<sub>10</sub> 155-65°, and III, b<sub>10</sub> 190-225°. II treated with PhONa in EtOH yields the liquid di-*p*-tolylmethane (IV), b<sub>10</sub> 158-63°, and a solid, diphenoxymethyltoluene (V), m 63-9°. V results from the reaction of PhONa on a dichloromethyltoluene probably identical with that (m. 43.5°) formed by condensing MeOCH<sub>2</sub>Cl with *p*-ClCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Me in the presence of SnCl<sub>4</sub>. III, by repeated fractionation, yields a chloromethyltolyltolylmethane, C<sub>12</sub>H<sub>12</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Cl.

I. P. ROLF

Nitration with nitrates. II. J. B. MENKE. *Rec. trav. chim.* 44, 269-70(1925).—In a previous paper (C. A. 19, 2191) a new method of nitration by the use of inorg. nitrates with Ac<sub>2</sub>O was described and it was stated that the reaction could be retarded by adding AcOH to the mixt. M. has now studied the action of inorg. nitrates in glacial AcOH alone. The results with various nitrates are of the same general character as were obtained with Ac<sub>2</sub>O except that with AcOH the reaction is much quieter. Ten g Cu(NO<sub>3</sub>)<sub>2</sub> with 25 g AcOH does not apparently react; if heated and distd. the distillate contains much N-O compds. but CH(NO<sub>2</sub>)<sub>2</sub> and C(NO<sub>2</sub>)<sub>4</sub> are not formed. Nitrations may be effected with this mixt. in which acetylorthonitric acid, in the nascent state, is thought to be the active agent. PhOH, *o*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>OH, PhNMe<sub>2</sub> were easily nitrated at low temps with both Cu(NO<sub>3</sub>)<sub>2</sub> and Fe(NO<sub>3</sub>)<sub>3</sub>. C<sub>6</sub>H<sub>6</sub> was scarcely acted upon at 105° and PhNHAc at 75°, while with the Ac<sub>2</sub>O procedure both are nitrated at 30°. The applications of the method are doubtless limited but interesting. Thus 5 g. PhOH in 10 g AcOH was added in 10 min. to 8 g. Cu(NO<sub>3</sub>)<sub>2</sub> in glacial AcOH, the temp. being

kept at 26°. Twenty min. after the addn. was complete the mixt. was poured into 100 cc. H<sub>2</sub>O and 5 g. pure *o*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>OH sepd. Thus only 1 of the 2 isomers usually obtained was formed in quantity.

E. J. WITZEMANN

**Substituted thioureas. V. The synthesis of thioureas from aminoethanols and of thiazolidine derivatives.** F. R. DAINS, R. L. BREWSTER, I. L. MALM, A. W. MILLER, R. V. MANEVAL AND J. A. SULTZBERGER. *J. Am. Chem. Soc.* 47, 1981-9 (1925); cf. C. A. 17, 281.—*p*-Xylylaminoethanol, *b*<sub>10</sub> 206°, *m*. 57°. *p*-Bromophenylaminoethanol *m*. 93°. The following thioureas were prepd.: *α*-*p*-Bromophenyl-*β*-*p*-tolyl, *m*. 184°; *α*-*p*-bromophenyl-*β*-*α*-naphthyl, *m*. 188°; *α*,*β*-di-*p*-xylyl, *m*. 155°; *α* phenyl-*β*-*p*-xylyl, *m*. 133°; *α*-*p*-tolyl-*β*-*p*-xylyl, *m*. 140°; *α*-*o*-tolyl-*β*-*p*-xylyl, *m*. 139°; *p*-xylyl, *m*. 141°. Diphenylethanolthiourea, *m*. 108°, from PhNCS and PhNHCH<sub>2</sub>CH<sub>2</sub>OH; heated with HCl, HBr, COCl<sub>2</sub> or other acid chloride it gives diphenylthiazolidine; heat alone also closed the ring, although the reaction was not smooth, HgO in C<sub>6</sub>H<sub>6</sub> gives diphenyl-oxazolidine; this also results from Pb(OH)<sub>2</sub> in EtOH with NH<sub>3</sub> or PhNH<sub>2</sub>; HOC<sub>6</sub>H<sub>4</sub>Cl in KOH also acts as a desulfurizing agent. The following derivs. of *α*-ethanol-*γ*,*β*-*R*,*R'*-thiourea were prepd.: *α*-phenyl-*β*-*p*-tolyl, *m*. 101°; *α*-*p*-tolyl-*β*-phenyl, *m*. 120°; *α*,*β*-di-*p*-tolyl, *m*. 130°; *α*-phenyl-*β*-*o*-tolyl, *m*. 91°; *α*-*p*-tolyl-*β*-*o*-tolyl, oil; *α*-phenyl-*β*-*o*-methoxyphenyl, oil; *α*-*o*-methoxyphenyl-*β*-phenyl, *m*. 143°; *α* phenyl-*β*-*α*-naphthyl, not purified; *α*-*p*-bromophenyl-*β* phenyl, *m*. 98°; *α*-phenyl-*β*-*p*-bromophenyl, *m*. 131°; *α*-*p*-tolyl-*β*-*p*-bromophenyl, *m*. 137°; *α* *p*-bromophenyl-*β*-*p*-tolyl, oil; *α*-*p*-bromophenyl-*β*-*α*-naphthyl, *m*. 60°; *α*-*α*-naphthyl-*β*-*p*-bromophenyl, oil; *α*-*p*-bromophenyl-*β*-allyl, *m*. 96°; *α*-*p*-xylyl-*β*-*p*-tolyl, *m*. 107°; *α*-*p*-xylyl-*β*-*o*-tolyl, oil; *α*-*p*-xylyl-*β*-*p*-xylyl, oil; *α*-phenyl-*β*-methyl, *m*. 69°; *α* methyl-*β*-phenyl, *m*. 95°; *α*-ethyl-*β*-phenyl, *m*. 152°; *α*-phenyl-*β*-ethyl, *m*. 97°; *α*-benzyl-*β*-phenyl, *m*. 110°; *α*-phenyl-*β*-benzyl, oil. Heating these with HCl gave derivs. of 2-*R*-amino-3-*R'*-thiazolidine as follows: 2-*p*-tolyl-3-phenyl, *m*. 113°; 2-phenyl-3-*p*-tolyl, *m*. 127°; 2,3-di-*p*-tolyl, *m*. 110°; 2-*o*-tolyl-3-*p*-tolyl, *m*. 110°; 2-phenyl-3-*o*-methoxyphenyl, *m*. 144°; 2-*o*-methoxyphenyl-3-phenyl, *m*. 103°; 2-*α*-naphthyl-3-phenyl, *m*. 130°; 2-phenyl-3-*p*-bromophenyl, *m*. 113°; 2-*p*-bromophenyl-3-phenyl, *m*. 112°; 2-*p*-bromophenyl-3-*p*-tolyl, *m*. 97°; 2-*p*-tolyl-3-*p*-bromophenyl, *m*. 145°; 2-*α*-naphthyl-3-*p*-bromophenyl, *m*. 127°; 2-*p*-bromophenyl-3-*α*-naphthyl, *m*. 165°; phenyl-*p*-xylyl, oil (picrate, *m*. 159°); 2-*p*-tolyl-3-xylyl, *m*. 112°; 2-*p*-xylyl-3-*p*-tolyl, *m*. 90°; 2-*α*-tolyl-3-*p*-xylyl, picrate, *m*. 179°; 2-*p*-xylyl-3-*o*-tolyl, picrate, *m*. 147°; 2,3-di-*p*-xylyl, *m*. 86°; 2,3-di-*p*-xylyl-5-methyl, picrate, *m*. 151°; 2-methyl-3-phenyl, *m*. 45°; 2-phenyl-3-methyl, *m*. 89°; 2-phenyl-3-ethyl, oil (perchlorate, *m*. 90°); 2-ethyl-3-phenyl, *m*. 42° (perchlorate, *m*. 68°); 2-phenyl-3-benzyl, *m*. 190°; 2-benzyl-3-phenyl, *m*. 85°. Some of these products are also formed by the action of C<sub>6</sub>H<sub>5</sub>Br, upon the thiourea contg. the 2 groups; where the 2 groups are unlike, 2 possible isomers may result, these reactions are discussed and the products isolated listed. The following dithioethylene ethers resulted when the alkyl-phenylthioureas were heated with C<sub>6</sub>H<sub>5</sub>Br<sub>2</sub> at 100° for 2 hrs.: phenylmethyl, *m*. 139°; HBr salt, *m*. 213°; phenylethyl, *m*. 130°, HBr salt, *m*. 196°; perchlorate, *m*. 160°, phenylbutyl, *m*. 92°; propylene ether of phenylmethyl, *m*. 120°; HBr salt, *m*. 195°. HgO and the ethanolthioureas gave the following 2,3-diaryloxazolidines: 2,3-diphenyl, *m*. 124°; di-*p*-tolyl, *m*. 136°; 2-phenyl-3-*p*-bromophenyl, *m*. 149°; 2-*p*-bromophenyl-3 phenyl, *m*. 138°; 2-*p*-bromophenyl-3-*p*-tolyl, *m*. 108°.

C. J. WEST

**Action of nitrous acid on azoxyphenols.** D. BIGIARI AND A. ANGELL. *Atti accad. Lincei* [v] 33, 319-22 (1924).—When a concd. Et<sub>2</sub>O soln. of *β*-*p*-azoxyphenol is satd. at 0° with the mixt. of N oxides from As<sub>2</sub>O<sub>3</sub> and HNO<sub>3</sub>, *m*-nitro-*β*-*p*-azoxyphenol, *m*. 174°, is produced (cf. Valori, C. A. 9, 1475). In the same way, *β*-*m*-azoxy-2-hydroxytoluene and *p*-nitrophenol yield, resp., benzene *β*-*m*-azoxy-2-hydroxy-3-nitrotoluene, *m*. 121°, and 2,4-dinitrophenol. HNO<sub>3</sub> from NaNO<sub>2</sub> however, reacts with none of these 3 (cf. C. A. 17, 1447); moreover, *α*-*p*-azoxyphenol, which gives only a mononitro deriv. with the latter reagent, is converted by the mixt. of N oxides into benzene *α*-*p*-azoxy-3,5-dinitrophenol, *m*. 197° (cf. C. A. 9, 1475). Azoxyphenols are usually oxidized by HNO<sub>3</sub>. Thus [*p*-HOC<sub>6</sub>H<sub>4</sub>N=] gives, not only a dinitroazoxyphenol, but also nitrophenol by oxidative fission (cf. C. A. 17, 2874). Benzene-*α*-azoxy-*α*-naphthol is likewise oxidized to a substance, *m*. 231°, contg. 10% of N. Benzene-*α*-azoxyquinol gives benzene-*α*-azoxy-*p*-benzoquinone. The mechanism of the formation of nitro derivs. by means of HNO<sub>3</sub> is discussed.

B. C. A.

**Synthesis of 2-hydroxy-3,5-dinitrobenzene arsonic acid and reduced products.** A. KEDATSU AND K. YOKOTA. *J. Pharm. Soc. Japan* No. 510, 629-36 (1924).—14 g. picramic acid and 140 cc. 40% HCl are shaken in a 3-necked flask and 5 g. NaNO<sub>2</sub> in a little H<sub>2</sub>O is added slowly (30 min.), at -10° and shaken for 1 hr. The product is then poured into 450 g. ice H<sub>2</sub>O. 15 g. of the diazo compd. is obtained. This compd. is suspended in 450 g. ice H<sub>2</sub>O and 35 cc. Schmit's arsenite soln. (168 g. As<sub>2</sub>O<sub>3</sub> and 800

cc 5 N KOH made up to 1 l) is added. While shaking, a small amt. of Cu powder is added. After 24 hrs, the mixt. is heated to 50°, and made acid with 14 g. 30% HCl. The small amorphous ppt. is then filtered off, the soln. decolorized and concd. *in vacuo*, and the product recrystd. from alc. The 2,3,5- $C_6H_3(OH)(NO_2)_3AsO_3H_2$  (I) thus obtained m. 273°, and is identical with that obtained by Benda from *p*-nitroaniline (C. A. 6, 490). According to B's method, the position of the 2nd nitro group is assumed to be next to OH, and K. and Y.'s method of synthesis from picramic acid confirm B's assumption. Attempts to obtain [2,3,5-HO(H<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>As=]<sub>2</sub> from I with Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> resulted in failure. If H<sub>3</sub>PO<sub>2</sub> is used as reducer, [HO(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>As=]<sub>2</sub> is formed. If the reduction is continued, only [HO(O<sub>2</sub>N)(H<sub>2</sub>N)C<sub>6</sub>H<sub>3</sub>As=]<sub>2</sub> is formed. The reduction with a mixt. of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> and H<sub>3</sub>PO<sub>2</sub> seemed to give the desired product, which, however, is so unstable that the method is not practicable. S. T.

**Mercurization of methylene blue.** LYMAN CHALKLEY, JR. *J. Am. Chem. Soc.* 47, 2055-61 (1925).—Because of the *in vitro* staining of tubercle bacilli by methylene blue (I) and the toxic effect of Hg salts, it seemed desirable to prep. a Hg salt of I. The Bz deriv. of leucomethylene blue in EtOH and 3 equivs. of Hg(OAc)<sub>2</sub> in dil. AcOH, boiled 20 min., cooled, filtered, the filtrate evapd. to dryness, suspended in H<sub>2</sub>O and extd. with C<sub>6</sub>H<sub>6</sub>, and the product pptd. twice from C<sub>6</sub>H<sub>6</sub> with HgO<sub>2</sub>, gave 52% of the *acetoxymercuri* deriv., powder with indefinite m. p.; H<sub>2</sub>S pptd. a fairly stable yellow sulfide. Dried over H<sub>2</sub>SO<sub>4</sub> it came to const. wt. in about a month, during which time some decompn. occurred. One mol. I is well sepd. from 6 mols. Hg(OAc)<sub>2</sub> by 3 successive pptns. with NaClO<sub>3</sub> or from 15 mols. by 4 pptns. This pptn. is not prevented by the presence of AcOH and unless the acid is very strong and the soln. is allowed to stand for some time, the I is not oxidized in such solns. I chloride, transformed into the acetate by HgOAc and then heated 10 hrs. with Hg(OAc)<sub>2</sub>, the product reduced with Fe(OH)<sub>2</sub> and purified with NaClO<sub>3</sub> (exact details given), gives a mixt. of 2 Hg derivs., one of which is a reversible colloid and may be C<sub>20</sub>H<sub>14</sub>N<sub>4</sub>ClS<sub>2</sub>Hg (yield about 5% of the I chloride used); the ppt. discarded in the prepn. of the 1st compd. yield about 0.5% of the 2nd, which may be C<sub>20</sub>H<sub>14</sub>N<sub>4</sub>SClHg. The work is complicated by the fact that I is easily converted into other dyes. It is further complicated by the incompleteness of the reaction, even in the presence of a considerable excess of Hg(OAc)<sub>2</sub>. C. J. W.

**Mercury derivatives of azo dyes.** A. PROSKOURIAKOFF AND GEO. W. RAIZISS. *J. Am. Chem. Soc.* 47, 1974-9 (1925).—Chrysoin K salt and Hg(OAc)<sub>2</sub> in H<sub>2</sub>O or EtOH give the orange-brown K salt of dihydroxymercuri-dihydroxyazobenzene-sulfonic acid (I), amorphous. Orange II as the Na salt in H<sub>2</sub>O gives dihydroxymercuri-azonaphthol-benzene-sulfonic acid (II); the H<sub>2</sub>O or dil. HCl soln., on being cooled, forms a thick, gelatinous mass, sol. in dil. NaOH. Orange II and Hg(OAc)<sub>2</sub> in MeOH give *mercuri-bis* [hydroxymercuri-β-naphtholbenzene-sulfonic acid], red amorphous powder. Tropaeolin Y gives dihydroxymercuri-hydroxyazobenzene-sulfonic acid, brownish red powder; di-Na salt, sol. in H<sub>2</sub>O. Alizarin yellow R gives *mercuri bis* [nilebenzeneazobenzene-sulfonic acid] (III), light brown powder, when either the free acid or the Na salt is used. The toxicity of these compds. is lower than that of inorg. Hg compds., but their bactericidal effect is also lower. The following figures give the max. tolerated dose, the lethal dose, the bacterial dln. *Staphylococcus aureus* and *Bacillus typhosus*: I, —, 0.008, —, —; II, 0.030, 0.040, 1:5000, 1:5000, III, —, 0.15, 1:40,000, 1:20,000; HgCl<sub>2</sub>, 0.002, 0.003, 1:114,000, 1:118,000, mercurochrome 220, 0.032, 0.040, 1:4000, 1:3000. C. J. WEST

**The solubility of the salts of certain aromatic sulfonic acids.** FRITZ EPHRAIM AND ALFRED PFISTER. *Helvetica Chim. Acta* 8, 229-41 (1925).—The solubilities of the various salts studied are listed below; the cryst. properties and decompn. (loss of H<sub>2</sub>O) are also in general briefly described. In the following tabulation the 1st figure refers to the no. mols. of H<sub>2</sub>O of crystn., the 2nd to the soly. in g./l. *Salts of PhSO<sub>3</sub>H*, at 20°: Ca, 1, 612.6; Cd, 7, 312.4; Zn, 6, 143.1; Mn, 6, 163.5; Sr, 1, 154.9; Ba, 1, 143.5; Fe, 6, 92.3; Mg, 6, 76.4; Co, 6, 77.8. *Salts of 2-C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H*, at 16.5°: NH<sub>4</sub>, —, 131.4 (25°); K, 0.5, 80.2; Na, —, 58.7 (25°); Ag, —, 17.2; Ca, 1, 19.9; Cu, 6, 10.5; Sr, 1, 8.80; Cd, 6, 8.72; Zn, 6, 4.62; Pb, 1, 5.41; Na, 6, 3.55; Mn, 6, 3.34; Ba, 1, 3.84; Co, 6, 2.56; Fe, 6, 2.40; Mg, 4, 2.00. *Salts of anthracene-1-sulfonic acid*, at 20°: Sr, 3, 1.16; Ag, —, 0.59; Mg, 4, 0.78; Ca, 3, 0.83; Ba, 3, 0.69; Zn, 3, 0.56; Mn, 3, 0.48; Co, 3, 0.39; Cu, 3, 0.27; Ni, 6, 0.25. *Salts of anthracene-2-sulfonic acid*, at 20°: Ag, —, 0.32; Ca, 1, 0.16; Mn, 6, 0.058; Cd, 6, 0.093; Mg, 4, 0.077; Cu, —, 0.083; Zn, 6, 0.074; Co, 6, 0.052; Ni, 6, 0.046; Ba, 1, 0.048. *Salts of 6,2-C<sub>10</sub>H<sub>6</sub>(OH)SO<sub>3</sub>H*, at 20°: Ba, 0, 17.42; Cd, 6-7, 16.51; Pb, 6, 18.14; Mg, 8, 9.64; Cu, 7 (approx.), 12.48; Mn, 8, 12.00; Sr, 6, 11.11; Zn, 8, 8.74; Ni, 8, 5.29; Co, 8, 5.00. *Salts of 5,1-ClC<sub>10</sub>H<sub>6</sub>SO<sub>3</sub>H*, at 20°: Zn, 4, 12.05; Cu, 4, 10.83; Ag, 0, 5.51; Mn, 1, 7.42; Co, 4, 7.09; Ni, 4, 6.18; Sr, 3, 5.51; Ca, 1, 3.73; Ba, 2, 2.75; Pb, 2, 2.00. WM. B. PLUMMER

Reaction between aryl sulfonates and organomagnesium halides. HENRY GILMAN, N. J. BEABER AND C. H. MYERS. *J. Am. Chem. Soc.* 47, 2047-52 (1925); cf. C. A. 19, 977. —Arylesters of  $p\text{-MeC}_6\text{H}_4\text{SO}_3\text{H}$  when refluxed in PhMe with aryl-MgX give sulfones and phenols. The reaction under like conditions with a large excess of alkyl-MgX gives some phenol, the aryl alkyl sulfide and unidentified compds which are probably sulfones formed by rearrangement.  $p\text{-MeC}_6\text{H}_4\text{SO}_3\text{Ph}$  and  $\text{PhMgBr}$  give 43.5%  $p\text{-MeC}_6\text{H}_4\text{SO}_2\text{Ph}$ ;  $p\text{-MeC}_6\text{H}_4\text{MgBr}$  gives 45.4% of  $(p\text{-MeC}_6\text{H}_4)_2\text{SO}_2$ ;  $p\text{-MeOC}_6\text{H}_4\text{MgBr}$  gives 82%  $p\text{-anisyl } p\text{-tolyl sulfone}$ , m.  $159^\circ$ ;  $\alpha\text{-C}_{10}\text{H}_7\text{MgBr}$  gives 71%  $\alpha\text{-naphthyl } p\text{-tolyl sulfone}$ , m.  $119^\circ$ .  $p\text{-MeC}_6\text{H}_4\text{SO}_3\text{C}_6\text{H}_4\text{Me-o}$  and  $\text{PhMgBr}$  give 42.7%  $p\text{-MeC}_6\text{H}_4\text{SO}_2\text{Ph}$ , while a 61% yield was obtained from di- $p,p'$ -biphenyl di- $p$  toluenesulfonate, m.  $189\text{--}90^\circ$  (21.2% yield from  $(\text{HOC}_6\text{H}_4)_2$  and  $p\text{-MeC}_6\text{H}_4\text{SO}_2\text{Cl}$ ). The reactions between  $p\text{-MeC}_6\text{H}_4\text{SO}_3\text{Ph}$  and  $\text{EtMgI}$ ,  $\text{BuMgBr}$ ,  $\text{iso-AmMgBr}$ ,  $\text{cyclohexane-MgCl}$  and  $\text{PhCH}_2\text{MgCl}$  are discussed.

C. J. WEST

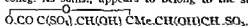
New method for the industrial preparation of picryl sulfide. MICHELE GIUA AND VITTORIO DE FRANCISCIS. *Ann. chim. applicata* 15, 137-45 (1925) —Substantially the same as C. A. 19, 1561.

C. C. DAVIS

Constitution of organic derivatives of sulfurous acid. F. RASCHIG. *Schwefel- u. Stickstoff-studien*, 1924, 242-9. —In the  $\omega\text{-SO}_2\text{H}$  acids formed from aldehyde-bisulfite compds, the S is linked directly to C, phenol and formaldehyde-bisulfite yielding the  $\text{SO}_2\text{H}$  acid,  $\text{HOC}_6\text{H}_4\text{CH}_2\text{SO}_2\text{H}$ . The compds. similarly obtained from amines such as aniline or  $\text{MeNH}_2$  are not true  $\text{SO}_2\text{H}$  acids, but are analogous in structure to formaldehyde-bisulfite itself, which has the structure  $\text{CH}_2\text{SO}_2\text{O}$  and contains the S only loosely attached. One O atom is readily removed by reduction, formaldehyde-bisulfite yielding "rongalite,"  $\text{CHNaSO}_2$ , in which the Na is attached directly to C. All aldehyde- and ketone-bisulfite compds. contain the metal directly bound to C, and the power of the  $\text{SO}_2$  group to make the H atoms attached to the neighboring C atom replaceable by metals decreases with the distance of the C atom to which the H is attached from the  $\text{SO}_2$  group.  $\text{Ph}_2\text{CO}$  gives no bisulfite compd. The compd. of phenanthraquinone with 1 mol. of  $\text{NaHSO}_3$  is attributed to the addn of water to the ketonic O atoms, giving the group  $\text{C}(\text{OH})_2$  in which a H atom of the HO groups is replaceable by metals. The third O atom in  $\text{H}_2\text{SO}_3$ ,  $\text{H}_2\text{SO}_3\text{:O}$ , plays a part in the replacement of amino groups in aromatic amines by HO groups in the presence of  $\text{H}_2\text{SO}_3$ ,  $\text{C}_{10}\text{H}_7\text{NH}_2$  yielding the intermediate compd.,  $\text{H}_2\text{SO}_3\text{:N-C}_{10}\text{H}_7$ , which changes to  $\text{HSO}_3\text{:NHC}_{10}\text{H}_7$ . In alk. soln., the tendency to replacement of the amino group by HIO is greater than the tendency to hydrolysis of the  $\text{SO}_2\text{H}$  group from N. In acid soln., the converse is true. The  $\text{N-SO}_2\text{H}$  acid of metanilic acid,  $\text{HO}_2\text{SC}_6\text{H}_4\text{NHSO}_2\text{H}$ , in alk. soln. yields  $m\text{-HOC}_6\text{H}_4\text{SO}_2\text{H}$  and aminosulfonic acid. Similarly, the formation of  $\text{H}_2\text{S}_2\text{O}_4$  by reduction of bisulfites with Zn is interpreted as reduction of the tautomeric form  $\text{H}_2\text{SO}_3\text{:O}$  to  $\text{H}_2\text{SO}_2$  and interaction of this with unchanged  $\text{H}_2\text{SO}_3$  yielding, by loss of water,  $\text{H}_2\text{SO}_4$ . The double linking of the 2 S atoms is easily split by the action of aldehydes, yielding mixts. of the aldehyde compds. of  $\text{H}_2\text{SO}_3$  and  $\text{H}_2\text{S}_2\text{O}_4$ .

B. C. A.

Action of sodium hypochlorite on  $p\text{-cresol}$ disulfonic acid. F. RASCHIG. *Schwefel- u. Stickstoff-studien* 1924, 250-4. — $p\text{-Cresol } 3,5\text{-disulfonic acid}$  with  $\text{NaClO}$  yields first a hypochlorous ester; the Cl then becomes detached from the O atom and enters the ring, 4 or 5 mols. of hypochlorite reacting with 1 mol. of di- $\text{SO}_2\text{H}$  acid. With 4 mols. of hypochlorite the benzene ring is opened and a substance is produced in which the strong single linking between C and S is converted into a weak double linking. The substance, which has the character of a HO acid and gives an odor of caramel on concg. its solns., appears to belong to the sugar group; it may have the formula



B. C. A.

Preparation and decomposition of unsymmetrical mercuri-organic compounds. A method of establishing the relative degree of negativity of organic radicals. M. S. KHARASCH AND MILDRED WATKINS GRAFFLIN. *J. Am. Chem. Soc.* 47, 1948-54 (1925). —*Methylmercuric 2,4,6-trinitrobenzoate*, m.  $165^\circ$  (decompn.), highly electrified and with a bitter taste, results in 4.3 g. yield from 3.6 g.  $2,4,6\text{-(O}_2\text{N)}_3\text{C}_6\text{H}_2\text{CO}_2\text{Ag}$  and 2.4 g.  $\text{MeHgCl}$ ; heated *in vacuo* at  $160\text{--}2^\circ$ ; it evolves  $\text{CO}_2$  giving  $[(\text{O}_2\text{N})_3\text{C}_6\text{H}_2]\text{Hg}$  and probably  $\text{HgMe}_2$ . The corresponding *phenylmercuric deriv.*, m.  $228^\circ$ , heated *in vacuo* at  $222^\circ$ , gives *phenylmercuric-2,4,6-trinitrophenyl*, cream powder, m.  $227.5^\circ$ . Its constitution was established by its reaction with  $\text{HgCl}_2$ , which yields  $\text{PhHgCl}$  and  $(\text{O}_2\text{N})_3\text{C}_6\text{H}_2\text{HgCl}$ . *p-Tolylmercuric 2,4,6-trinitrobenzoate*, grayish white, m.  $234\text{--}7^\circ$ ; elimination of  $\text{CO}_2$  gives *p-tolylmercuric-2,4,6-trinitrophenyl*, orange-tan, m.  $203^\circ$ ;  $\text{HgCl}_2$  gives  $\text{MeC}_6\text{H}_4\text{HgCl}$  and  $(\text{O}_2\text{N})_3\text{C}_6\text{H}_2\text{HgCl}$ . Decompn. of these compds. with  $\text{HCl}$  gives  $\text{C}_6\text{H}_6$  and  $\text{PhMe}$ , resp., and  $(\text{O}_2\text{N})_3\text{C}_6\text{H}_2\text{HgCl}$ , indicating that both the Ph and  $\text{MeC}_6\text{H}_4$  groups are more negative

than the  $(O_2N)_2C_6H_2$  group and that the introduction of  $NO_2$  groups into the  $C_6H_2$  ring weakens the electronegativity of the radical. C. J. WEST

Action of hydrogen sulfit and sulfit on nitro and nitroso compounds. F. RASCHIG. *Schwefel- u. Stickstoffstudien* 1924, 255-72.—The action of  $NaHSO_3$  on nitro compds. yields phenols and amines and their  $SO_3H$  acids, the  $SO_3H$  group in the *N*-monosulfonated amines,  $RNHSO_3H$ , being more firmly attached to N than this to C. When  $N O_2NC_4H_9SO_3Na$  reacts with 5 *N*  $NaHSO_3$ , the latter substance disappears in 4 hrs. at the ordinary temp.; the first product appears to be a condensation product,  $RN(O)(OH)SO_3Na$  or  $RN(O OH)SO_3Na$ .  $H_2SO_4$  appears after 10 hrs., and the reaction is incomplete after 8 days. Free  $H_2SO_4$  is then present in place of the sulfit. If  $2/3$  of the  $NaHSO_3$  is neutralized with  $NaOH$ , the reaction is much more rapid and after 6 hrs. only a little  $NaHSO_3$  is present with the disulfonate,  $RN(SO_3Na)_2$ . A substance,  $C_4H_7(SO_3Na)_2NHHSO_3Na \cdot 5H_2O$ , has been qual. detected, in which 2  $SO_3H$  groups occupy *o*-positions with respect to N.  $HO(H_2N)C_6H_4SO_3H$  is also formed. Dinitromesitylenesulfonic acid gives nitroaminomesitylenesulfonic acid and on warming a sol tri- $SO_3H$  acid, in which 2  $SO_3H$  groups are attached to N and at the same time an aminohydroxymesitylenesulfonic acid is formed. *m*- $ONC_6H_4SO_3H$  similarly yields as a first reaction product a condensation product,  $NaO_2SC_6H_4N(SO_3Na)_2$ , the liquid becoming acid during the reaction, which is thereby retarded. Treatment with  $HCl$  gives metanilic acid. *m*- $HONHC_6H_4SO_3H$  yields benzidinesulfonic acid, probably through the intermediate formation of the hydrazobenzene-sulfonic acid  $HONHC_6H_4SO_3Na$  is prep'd. by reduction of *m*- $O_2NC_6H_4SO_3Na$  with Zn dust in alc. at 74-80°. Excess of  $KMnO_4$  oxidizes it back to  $O_2NC_6H_4SO_3H$ , air only to the  $ONC_6H_4SO_3H$ . B. C. A.

Analogies between some reactions of organic peroxides and diazo compounds. H. GELLISSSEN AND P. H. HERMANS. *Ber.* 58B, 984-7 (1925)—Brief discussion.

C. A. R.

Asymmetric catalytic racemization. ALEX. MCKENZIE AND ISOBEL AGNES SMITH. *Ber.* 58B, 894-908 (1925); cf. C. A. 18, 3370, and earlier papers.—When esters of an optically active acid of the type  $PhCHNCO_2H$  are hydrolyzed with alc. KOH there is always more or less racemization, the factors conditioning this racemization being the presence of an aromatic residue and of a H atom in direct union with the asym. C atom. Likewise, if such esters are only partially hydrolyzed, the unsapon. part is also found to have undergone more or less racemization. It is believed that in the 1st stage of the hydrolysis there is formed an unstable complex between the ester and the KOEt and that it is only after the formation of this complex that the migratory property of the H atom comes into play, the KOEt thus exerting a catalytic action. The present paper describes the continuation, with the bornyl esters, of the earlier work on the menthyl esters of  $PhCHClCO_2H$  (I). The *l*-ester of *d*-I on crystn. from alc. undergoes resolution and this affords a method of obtaining the esters of the *d*- and *l*-acids. While pure *l*-I shows  $[\alpha]_D -153.8^\circ$  (alc.,  $c$  2.002), the acid obtained by sapon. of the *l*-bornyl ester with a slight excess of alc. KOH at room temp. shows  $[\alpha]_D 1^\circ$  (alc.,  $c$  9.826). The ester itself has  $[\alpha]_D -98.7^\circ$  (alc.,  $c$  1.2816) and if it is treated at room temp. with 0.5 the amt. of alc. KOH calcd. for complete hydrolysis, the non-hydrolyzed part shows  $[\alpha]_D -31.9^\circ$  (alc.,  $c$  1.318), corresponding to a mixt. of 51% *l*-I ester and 49% *d*-I ester. An identical mixt. is obtained when a single drop of alc. KOH is added to the pure *l*-I ester. In fact, the catalytic racemization at the beginning of the reaction is extraordinarily rapid; the original rotation,  $\alpha_D -261^\circ$ , falls to  $-216^\circ$  within 1.5 min. after adding a drop of alc. KOH. The pure *d*-I ester has  $[\alpha]_D 38.6^\circ$  (alc.,  $c$  1.3972) and 1 min. after adding 3 drops alc. KOH to a soln. with  $\alpha_D 1^\circ$ , the rotation changes to  $-0.37^\circ$  and in 15 min. attains a const. value of  $-0.95^\circ$ , corresponding to a mixt. of 48% *d*-I ester and 52% *l*-I ester. Similarly the *d*-bornyl ester of *d*-I gives with 1 drop of alc. KOH 53% and 47% of the *d*- and *l*-I esters, resp., and the ester of *l*-I with 3 drops alc. KOH gives 48% and 52% of the *l*- and *d*-I esters. Similarly, when the *l*-bornyl ester of *l*- $PhCHBrCO_2H$  is treated with 3 drops alc. KOH,  $[\alpha]_D$  changes in 3 hrs. from  $-98.5^\circ$  to  $-28^\circ$ . It had already been shown that when the *l*-menthyl ester of *l*-I is treated with 1 drop alc. KOH  $[\alpha]_D$  changes from  $-149.8^\circ$  to  $-86^\circ$ , it has now been found that the same value is obtained from the *d*-I ester ( $[\alpha]_D 5.6^\circ$ ) on similar treatment. As the *d*-I has  $[\alpha]_D -72.2^\circ$ , the result of the catalytic action of the KOEt is the formation of a mixt. in which the *l*-I ester predominates, thus furnishing an example of asym. catalytic racemization. Apparently the menthyl group exerts a directive influence on the desmotropism. With *l*- $PhCH(OH)CO_2Et$ , on the other hand, the Et group exerts no such directive influence and the catalytic racemization (sym. in this case) results in the formation of equal parts of the *d*- and *l*-esters. A logical deduction from the above observations is that the directive influence of an optically active terpene group may be

used to convert quant a mixt of equal parts of diastereoisomeric esters into a mixt. of unequal parts of these esters, and as a matter of fact a 1:1 mixt. of the *l*-menthyl esters of *l*- and *d*-1 gave with 1 drop of alc. KOH a 57:43 mixt.,  $[\alpha]_D$  changing in 35 min. from  $-2.09^\circ$  to  $-2.40^\circ$ ; a similar result was obtained with the *l*-menthyl esters of *d*- and *l*-PhCHBrCO<sub>2</sub>H and with the *d*-bornyl ester of *d*-L. The *l*-menthyl ester of *d*-L-PhCH(OH)CO<sub>2</sub>H with 3 drops alc. KOH gives a 46:54 mixt. of the esters of the *l*- and *d*-acids, although much more slowly than in the above cases (28 hrs.). *l*-Bornyl ester of *l*-1, m. 97.5–8.5°,  $[\alpha]_D^{15} -98.7^\circ$  (alc.,  $\epsilon$  1.2816),  $-102.6^\circ$  (C<sub>6</sub>H<sub>6</sub>,  $\epsilon$  2.1872),  $[\alpha]_{5461}^{15} -116.3^\circ$  (alc.),  $-120.9^\circ$  (C<sub>6</sub>H<sub>6</sub>), of *d*-1, m. 53–4°,  $[\alpha]_D^{15} 38.6^\circ$ ,  $[\alpha]_{5461}^{15} 45.8^\circ$  (alc.,  $\epsilon$  1.3972) *d*-Bornyl ester of *d*-1, m. 97.5–8.5°,  $[\alpha]_D^{15} 99.1^\circ$  (alc.,  $\epsilon$  1.2104); of *l*-1, m. 53–4°,  $[\alpha]_{5461}^{15} -44.8^\circ$  (alc.,  $\epsilon$  1.7652) *l*-Bornyl ester of *l*-PhCHBrCO<sub>2</sub>H, m. 91.5–2.5°,  $[\alpha]_D^{15} -95.8^\circ$ ,  $[\alpha]_{5461}^{15} -113.7^\circ$  (alc.,  $\epsilon$  1.3408);  $[\alpha]_D^{15} -101.1^\circ$ ,  $[\alpha]_{5461}^{15} -122.3^\circ$  (C<sub>6</sub>H<sub>6</sub>,  $\epsilon$  2.78). C. A. R.

**Tubaic acid.** T. KARIYONE AND S. KONDO. *J. Pharm. Soc. Japan* No. 518, 376–9 (1925).—According to Takei, tubaic acid (m. 129°), obtained by treating rotenone with alc. KOH has the compn. C<sub>19</sub>H<sub>19</sub>O<sub>8</sub>, while K. and K. found it to be C<sub>19</sub>H<sub>19</sub>O<sub>8</sub> (C. A. 18, 685). Re-analysis of this acid, with a larger quantity, gives the compn. C<sub>19</sub>H<sub>19</sub>O<sub>8</sub>, which is also confirmed by re-analysis of Ac deriv. Thus dihydrotubaic acid should be C<sub>19</sub>H<sub>19</sub>O<sub>8</sub>. According to T., a compd. obtained by alk. fusion of rotenone or tubaic acid is C<sub>19</sub>H<sub>19</sub>O<sub>8</sub> and was named by T. rotenic acid. K. and K. found this compd. is C<sub>19</sub>H<sub>19</sub>O<sub>8</sub> and is an isomer of tubaic acid. The analysis of its mono-Ac deriv. obtained by heating the compd. with NaAcO and Ac<sub>2</sub>O also confirms the correctness of this formula. This compd., therefore, could not be a dimethylsalicylic acid, as suggested by T. S. T.

**Phenylbis[phenylcyanomethoxy]methane, PhCH[OCH(CN)Ph]<sub>2</sub>.** R. STOLLÉ. *Ber.* 58B, 975 (1925).—Wood and Lilley's supposed PhCH(OH)NC (C. A. 19, 1134), obtained by allowing PhCH(OH)CN to stand, is really the above compd. (cf. *Ber.* 35, 1590 (1902); Savelsberg, C. A. 12, 1967). Their compd. and its alleged reduction product, PhCH(OH)NHMe, should not be allowed to remain in the literature. C. A. R.

**Kakishibu. III. Constitution of shibuol (2).** SHIGERU KOMATSU AND NAOKIYO MATSUNAMI. *Mem. Coll. Sci. Kyoto Imp. Univ.* 8A, 231–40 (1925).—Insol. shibuol (I), heated with H<sub>2</sub>O in a sealed tube at 125–30° for 10 hrs., is converted into a sol. form (II), which may be sepd. into 2 parts by cold H<sub>2</sub>O; the sol. part contains 10% ash (mostly Ca), the insol. part 0.2% ash. It is thought that some of the mineral matters in the fruit may play a part in keeping shibuol in a sol. form in the plant tissues. If in dil. HCl is partly decompd. in 24 hrs. into gallic acid (III) and partly transformed into I and phlobaphene (IV). Boiling, dil. H<sub>2</sub>SO<sub>4</sub> gives about 2% III and 98% IV. IV was also obtained from I by the action of (CO<sub>2</sub>H)<sub>2</sub> or with Mg–Hg in EtOH–HCl. Tetraacetylshibuol, by boiling with Ac<sub>2</sub>O, with or without pressure, exists in a sol. and an insol. form; it is completely decompd. into I and AcOH by heating with H<sub>2</sub>O at 150° for 10 hrs. or with MgO and H<sub>2</sub>O. Acetylation of IV in an open vessel gives a *di*-Ac deriv., while heating under pressure gives a *tri*-Ac deriv. Both are hydrolyzed by heating with H<sub>2</sub>O in a sealed tube at 135° for 10 hrs. C. J. WEST

**Reactivity of the methylene group in coumarin-4-acetic acids.** II. BEMAN BIHARI DRY AND KARNAD KRISHNA ROW. *Quart. J. Indian Chem. Soc.* 1, 277–87 (1925); cf. C. A. 19, 823.—*p*-MeOCH<sub>2</sub>CH=O and 7-methylcoumarin-4-acetic acid (I), heated with C<sub>6</sub>H<sub>11</sub>N at 130–5° for 4 hrs., give 7-methyl-4-coumaryl-*p*-methoxyphenylethylene (II), pale yellow, m. 180°; the concd. H<sub>2</sub>SO<sub>4</sub> soln. is deep red.  $\alpha$ -Naphthopyrone-4-*p*-methoxyphenylethylene, bright yellow, m. 182–3°; it decolorizes Br in CHCl<sub>3</sub>. I and vanillin give 7-methyl-4-coumaryl-3'-methoxy-4'-hydroxyphenylethylene, golden yellow, m. 222°. I and *p*-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CHO give the corresponding *p*-dimethylamino deriv. of II, orange, m. 190°; picrate, yellow, m. 204° and then decomp. with a small explosion; HgCl<sub>2</sub> salt, prisms; dichromate, chocolate-brown; chloroplatinate, pale yellow; ferrocyanide, light green.  $\alpha$ -Naphthopyrone-4-*p*-dimethylaminophenylethylene, deep red, m. 215–6°; HCl salt, needles, gradually dissociated by H<sub>2</sub>O. Vanillin, PhCH<sub>2</sub>CO<sub>2</sub>Na and Ac<sub>2</sub>O, heated 6 hrs., give 4-hydroxy-3-methoxystilbene- $\alpha'$ -carboxylic acid (III), sinters 181°. m. 186–7°. Vanillin, PhCH<sub>2</sub>CO<sub>2</sub>H and C<sub>6</sub>H<sub>11</sub>N give 4-hydroxy-3-methoxystilbene, m. 134°; the 2 N NaOH soln. has a pale yellow tint and develops a blue fluorescence on diln. 3,4-Dimethoxystilbene, m. 111°. 5-Bromovanillin gives the 5-Br deriv. of III, m. 222°. 4-Hydroxy-3-methoxy-2',4'-dinitrostilbene, deep red, m. 193°; on addn. of alkali, it turns black; on warming it slowly gives a dark brown soln.; acids ppt. the original red substance. *p*-Dimethylaminostilbene, m. 150°; the HCl salt m. 174° and dissolves in a large excess of H<sub>2</sub>O without appreciable dissociation. Methylene ether of

3,4-dihydroxystilbene- $\alpha'$ -carboxylic acid, m. 231-2°; Ag salt, Et ester, m 104°. Methylene ether of 3,4-dihydroxystilbene, m 95-6°; dibromide, m 187° (cf. Hell and Wiegandt, *Ber* 37, 1431(1904)); 2',4'-dinitro deriv., reddish brown, m 183°. C. J. West

Preparation of 3-nitrophthalic acid. E. R. LITTMANN *J. Am. Chem. Soc.* 47, 1980-1(1925) —  $\text{HNO}_3$  (d 1.42) (175 cc.) and 185 g. of  $\text{C}_6\text{H}_5(\text{CO})_2\text{O}$ , thoroughly mixed, are treated with 175 cc  $\text{H}_2\text{SO}_4$  (d 1.84) with const. shaking and the mixt is heated 2.5-3 hrs on the steam bath. The contents are then poured into 500 cc.  $\text{H}_2\text{O}$ , the crude product is mixed with 600 cc  $\text{C}_6\text{H}_6$  and distd until about 300 cc. have passed over (distillate no longer turbid), this gives on cooling 85-90% of a product m. 198° and having a neutral equiv. of 200 Recrystd. from glacial  $\text{AcOH}$ , it m 206°. C. J. W.

New method for the preparation of 4'-hydroxydiphenylmethane-2-carboxylic acid. R. KONDO AND Y. MIYASHITA. *J. Pharm. Soc. Japan* No. 510, 643-9(1924).—5 g. of dry  $\alpha\text{-NCC}_6\text{H}_4\text{CH}_2\text{Cl}$  and 9 g.  $\text{PhOH}$  are placed in a flask and well stirred. The clear transparent mixt is heated, protected from moisture by  $\text{CaCl}_2$ , with 2 g.  $\text{Zn}$  dust at 115-20°;  $\text{HCl}$  is given off. Heating is continued at 130° for 3-4 hrs till  $\text{HCl}$  is no longer evolved. The mixt becomes a red brown mass, from which the excess of  $\text{Zn}$  dust and  $\text{ZnCl}_2$  are removed, and is extd with acetone. After removing the acetone,  $\text{H}_2\text{O}$  is added, the  $\text{PhOH}$  is distd. off by steam, and the mixt. filtered hot. The brownish resinous ppt is washed with hot  $\text{H}_2\text{O}$ . The filtrate and the wash  $\text{H}_2\text{O}$  are combined, evapd., and cooled; crystals, m 130°, of 2-cyano-4'-hydroxydiphenylmethane,  $\alpha$ -( $\text{p-HOC}_6\text{H}_4\text{CH}_2$ ) $\text{C}_6\text{H}_4\text{CN}$  (47 g.) are obtained. When 3 g. of this is hydrolyzed with 30 cc. alkali (1.5) at 120-30° under a reflux, 1.8 g. of  $\alpha$ -( $\text{p-HOC}_6\text{H}_4\text{CH}_2$ ) $\text{C}_6\text{H}_4\text{CO}_2\text{H}$  is obtained identical with that prepd. by Bistrzycki's method (*Ber* 27, 2632(1894)). Its cor. m p is 148-50°, not 145-6° as B. reports S. T.

Electrochemical relation of free radicals to halochromic salts. J. B. CONANT, L. F. SMALL AND B. S. TAYLOR. *J. Am. Chem. Soc.* 47, 1959-74(1925).—Mixts. of  $\text{Ph}_3\text{C}(\text{Ph}_2\text{CCPh}_2)$  and  $\text{Ph}_3\text{CSO}_3\text{H}$  in glacial  $\text{AcOH}$  give reproducible potentials which accord with the usual electrochem. equations. The single electrode potentials of  $\text{Ph}_3\text{C}$ , phenylxanthyl and phenyldimethoxyxanthyl have been measured by a titration method in  $\text{AcOH}$  and  $\text{Me}_2\text{CO}$  solns. of varying acidity. A method has also been developed of estg. the activity of the  $\text{H}$  ion in non-aq. solvents by means of oxidation-reduction cells involving tetrachloroquinone (chloranil). The changes of the electrode potentials of the free radicals with change in  $\text{H}$ -ion activity of the solns. are in accord with an electrochem. equation which has been derived. A convenient method of prepg. dissociated and undissociated ethanes directly from the carbinols consists in dissolving them in a suitable solvent contg. a certain amt. of acid, adding a concd. aq. soln. of vanadous salt and, after the reaction is complete, pptg. with  $\text{H}_2\text{O}$ .  $\text{TiCl}_4$  may be used but is a much less general reagent than  $\text{VCl}_4$ . A no. of examples are given C. J. WEST

3',3'',3'''-Trimethylaurin ( $\alpha$ -cresaurin) and 3',3'',3'''-trimethyl- $\text{N}^1, \text{N}^2, \text{N}^3$ -triphenyl- $\text{p}$ -rosaniline (triphenyl- $\text{ros-o}$ -toluidine). M. GOMBERG AND L. C. ANDERSON. *J. Am. Chem. Soc.* 47, 2022-33(1925).—The condensation of  $\alpha\text{-MeC}_6\text{H}_4\text{OH}$  with  $\text{CCl}_4$  in the presence of  $\text{ZnCl}_2$  (125°),  $\text{AlCl}_3$  (100°) or  $\text{SnCl}_4$  (autoclave at 130°) gives ( $\alpha\text{-MeC}_6\text{H}_4$ ) $\text{CO}_2\text{H}$ , 3',3'-dimethyl-4',4'-dihydroxybenzophenone (I), light pink, m 240° (di-Ac deriv., m 102°), and  $\alpha$ -cresaurin (II), maroon color. Schroeter (*Ann.* 257, 74(1890)), who supposed he had I from the fusion of  $\alpha$ -cresolbenzene and  $\text{KOH}$ , actually had 3,4-Me( $\text{HO}$ ) $\text{-C}_6\text{H}_4\text{COPh}$ , m 163° (Ac deriv., m 68°). Di-MeO deriv. (III), of I, m 116°, prepd. by methylating I and by the action of 3,4-Me( $\text{MeO}$ ) $\text{C}_6\text{H}_3\text{CHO}$  upon 3,4-Me( $\text{MeO}$ ) $\text{C}_6\text{H}_3\text{-MgBr}$  and oxidation of the hydrol. Its oxime, m 137°  $\alpha\text{-MeC}_6\text{H}_4\text{OH}$  and ( $\text{CO}_2\text{H}$ ) $_2$  with  $\text{H}_2\text{SO}_4$  gave 39-42% of pure dye, with  $\text{H}_3\text{PO}_4$  the condensation was very slow and the yields poor.  $\alpha\text{-MeC}_6\text{H}_4\text{OK}$  and  $\text{CCl}_4$  (Baines and Driver, *C. A.* 17, 2575) gave from 7-11% II.  $\text{Ros-o}$ -toluidine gave 18% II. II is very sol in  $\text{NH}_4\text{OH}$  and the alkali and alk. earth hydroxides with a dark wine color. Heavy metal hydroxides give very slightly sol lakes. II,  $\text{AcOH}$  and  $\text{AcONa}$  give 3',3'',3'''-trimethyl-4',4'',4'''-triaceoxy-triphenylcarbinol, m 141°; II,  $\text{Zn}$  and  $\text{AcOH}$  give the trimethyltri-hydroxytriphenylmethane, m 200°. The *tri-MeO* carbinol, m 157°, results by methylating II or from III and 3,4-Me( $\text{MeO}$ ) $\text{C}_6\text{H}_3\text{MgBr}$ , chloride, m 164°; peroxide, m 161-2°. The tribenzyloxy-carbinol, m 182°. II and Br in glacial  $\text{AcOH}$  give a di-Br deriv., maroon colored. Oxidation of II gives 41% I. II forms salts with  $\text{HCl}$ ,  $\text{HBr}$  and  $\text{HClO}_4$  and yields an acid and normal sulfate. II,  $\text{PhNH}_2$  and  $\text{C}_{10}\text{H}_8\text{O}_2$ ,  $\text{ros-o}$ -toluidine,  $\text{PhNH}_2$ , and  $\text{BzOH}$  or  $\text{C}_{11}\text{H}_{10}\text{O}_2$ ; or II tri-Me ether,  $\text{PhNH}_2$  and  $\text{C}_{10}\text{H}_8\text{O}_2$  give triphenyl- $\text{ros-o}$ -toluidine ( $\text{N}^1, \text{N}^2, \text{N}^3$ -triphenyl-4',4'',4'''-tri-*aurin*-3',3'',3'''-triphenylcarbinol chloride), bronze-colored, which absorbs 1 or 2 additional mols. of  $\text{HCl}$  in dry  $\text{HCl}$  but loses them at 80° *in vacuo*; alkali ppts a light colored carbinol, which yields the chloride with  $\text{HCl}$ ; picric acid gives a very slightly sol picrate. The corresponding methane, m 178-80°. Other blue dyes

have been prepd. by condensing  $\alpha$ -C<sub>10</sub>H<sub>7</sub>NH<sub>2</sub>,  $\beta$ -C<sub>10</sub>H<sub>7</sub>NH<sub>2</sub> or  $p$ -H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>Ph with the tri-Me ether of II. "New Fuchsin," which is a mixt of several substances, contains, as has been surmised, ros o-toluidine, which has been isolated and its constitution established by converting it into II.

C. J. WEST

Condensation of chloroform, carbon tetrachloride and iodoform with resorcinol and other similar hydroxy aromatic compounds. RAJENORA NATH SEN, NRIPENDRA NATH SINHA AND NRIPENDRA NATH SARKAR *Quart J Indian Chem. Soc.* 1, 303-6 (1925); cf. *C. A.* 19, 2196 —  $m$ -C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub> and CHCl<sub>3</sub>, CHI<sub>3</sub> or CCl<sub>4</sub> with ZnCl<sub>2</sub> give *resorcin-o,p*-dihydroxybenzoin, C<sub>11</sub>H<sub>12</sub>O<sub>3</sub>, orange-yellow, does not m below 290°, gives a red soln. with a green fluorescence in alkali, dyes wool and silk orange shades. *Tetra-Br deriv.*, dyes wool and silk red shades. 1,2,3-C<sub>6</sub>H<sub>3</sub>(OH)<sub>3</sub> and CHCl<sub>3</sub> or CHI<sub>3</sub> with ZnCl<sub>2</sub> give *pyrogallol-o,m*-*p*-trihydroxybenzoin, black, does not m below 250°, sol in alkali without fluorescence. CHI<sub>3</sub> and  $p$ -C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub> give *hydroquinol-o,m'*-dihydroxybenzoin, does not m. below 250°, sol in alkali with red color and faint blue fluorescence, and in EtOH and Me<sub>2</sub>CO with a green fluorescence.

C. J. WEST

Nitro derivatives of 2-methylnaphthalene. V. VESELY AND J. KAPP *Chem. Listy* 18, 201-5, 244-9 (1924), cf. *C. A.* 18, 233-4 — When 2-C<sub>10</sub>H<sub>7</sub>Me is nitrated to the mononitro stage 4 derive can be isolated or characterized. The crude mixt is reduced with alc. (NH<sub>4</sub>)<sub>2</sub>S, 1,2-C<sub>10</sub>H<sub>6</sub>(NO<sub>2</sub>)NH<sub>2</sub>, the chief product and the only one isolated hitherto (cf. Schulze, *Ber.* 17, 842-6, Lesser, Glaser and Aczel, *C. A.* 8, 661) remains unattacked. The mixt of amines obtained is semi solid and when filtered affords 6(?) amino-2-methylnaphthalene, m 123° (*Ac deriv.*, m 153°, *Bz deriv.*, m 182-3°), the corresponding 2-methyl-6(?) naphthol, m 125.5°. The residual oily amine is either acetylated or benzoyleated and then fractionally crystd from alc., it thus affords 4-amino-2-methylnaphthalene, m 51-2°, as the *Ac deriv.*, m 175-6°, or 8-amino-2-methylnaphthalene as the *Bz deriv.*, m 194-5°. 1,3-C<sub>10</sub>H<sub>6</sub>(NH<sub>2</sub>)Me was prepd for comparison as follows. 1,2-C<sub>10</sub>H<sub>6</sub>(NHAc)Me (Lesser, *loc cit*) is nitrated, and the resulting 4-nitro-1-acetamino-2-methylnaphthalene, m. 240-1°, hydrolyzed to 4-nitro-2-methyl- $\alpha$ -naphthylamine, m 184-5°, which, by displacement of the amino group in the usual way, affords 4,2-C<sub>10</sub>H<sub>6</sub>(NO<sub>2</sub>)NH<sub>2</sub>, m. 49-50°. Reduction now yields the desired amine, the *Bz deriv.* of which m. 188-9°. By the usual methods it affords 1,3-C<sub>10</sub>H<sub>6</sub>(OH)Me and 4-bromo-2-methylnaphthalene (*picrate*, m. 90-1°). 1,4,2-C<sub>10</sub>H<sub>6</sub>(NH<sub>2</sub>)(NO<sub>2</sub>)Me, when reduced, affords 1,4-diamino-2-methylnaphthalene, m. 111-3°, which is converted by oxidation into 2-methyl- $\alpha$ -naphthoquinone (Fries and Lohmann, *C. A.* 16, 1419). 1,7-C<sub>10</sub>H<sub>6</sub>(NH<sub>2</sub>)Me (*Ac deriv.*, m. 175-6°) is converted in the usual way into 1,7-C<sub>10</sub>H<sub>6</sub>(OH)Me (Krollpfeiffer and Schäfer, *C. A.* 17, 2422) and its constitution thus established. It also affords 8-bromo-2-methylnaphthalene, an oil (*picrate*, m. 99-100°). When 2-C<sub>10</sub>H<sub>7</sub>Me is dinitrated, "mixed acid" being used, it yields at least 2 dinitro derivs. The 1,8(?), m. 209°, has already been described by Schulze and by Lesser (*loc cit.*). The 2nd product is 1,5-dinitro-2-methylnaphthalene, m 131°. Its constitution was detd. as follows. On reduction with alc. (NH<sub>4</sub>)<sub>2</sub>S, it affords 1-nitro-(5)-amino-2-methylnaphthalene, m. 134-5° (*Ac deriv.*, m 192°). This is converted into (5)-bromo-1-nitro-2-methylnaphthalene, m 94° [cf. the product obtained by Lesser (*loc cit.*), by brominating 1,2-C<sub>10</sub>H<sub>6</sub>(NO<sub>2</sub>)Me], and, further, into (5)-bromo-2-methyl- $\alpha$ -naphthylamine, m. 53.5° (*Ac deriv.*, m. 184-5°), and so into (5)-bromo-2-methyl- $\alpha$ -naphthol, m. 78-9°. The latter affords 3-bromophthalic acid on oxidation. The Br atom must therefore be in the 5- or in the 8-position in the original C<sub>10</sub>H<sub>7</sub> nucleus. From the 1,(5),2-C<sub>10</sub>H<sub>6</sub>(NH<sub>2</sub>)-BrMe described above, the amino group was displaced. The product was different from the 8,2-C<sub>10</sub>H<sub>6</sub>BrMe previously described, and was therefore certified to be 5-bromo-2-methylnaphthalene (*picrate*, m. 91-2°). 1,5-Diamino-2-methylnaphthalene, m 125-S°.

B. C. A.

1-Arylamino-2-naphthoquinones. R. LANTZ AND A. WAHL. *Compt. rend.* 180, 1351-4 (1925). — By duplicating with 8% aq. of NaOCl, the oxidation of weakly alk. EtOH solns. of 1-arylamino-2-hydroxynaphthalenes, which occurs spontaneously on the shaking with air, quant yields of the emerald-green needles of the quinones are formed. With the Ph deriv. the product (m. 100°), is the 1-phenylimino-2-naphthoquinone of Euler (*Ber.* 39, 1040). 1-[*o*-Methoxyphenylimino]-2-naphthoquinone and 1-[*p*-acetylaminophenylimino]-2-naphthoquinone were prepd. The great instability of these quinones limits their value. A mistake in the formula of Euler (Astrid and Euler, *Ber.* 39, 1041) is pointed out.

I. P. ROLF

Aryliminonaphthoquinones. Action of aromatic amines. R. LANTZ AND A. WAHL. *Compt. rend.* 180, 1509-12 (1925). — 1-Phenylimino-2-naphthoquinone (I) added to PhNH<sub>2</sub> in Et<sub>2</sub>CO at room temp deposits brown crystals, C<sub>18</sub>H<sub>16</sub>ON<sub>2</sub> (II), in 50% yield, and simultaneously I is reduced by the freed H<sub>2</sub> to 1,2-C<sub>10</sub>H<sub>6</sub>(NHPh)OH. That the PhN-

grouping in II is *p*- to the original PhN— is proved by boiling for 20 min. with dil. HCl, giving 2-hydroxy-4-phenyliminonaphthoquinone (*Ber.* 27, 25). A tautomerism probably exists in II between 2-hydroxy-1,4-diphenyliminonaphthoquinone and 1-phenylimino-4-phenylamino-2-naphthoquinone. II is distinguished from its known isomer, 2-phenylamino-4-phenyliminonaphthoquinone (into which it is transformed by boiling with HOAc), by its greater stability toward acids, its solubilities, and the color of its H<sub>2</sub>SO<sub>4</sub> soln.

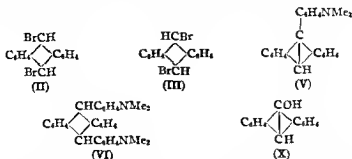
I. P. ROLF

Diphenysuccindene series. IX. 9,12-Diaryl-10-diphenysuccindene and 9,12-diaryldiphenysuccindane. K. BRAND AND WILHELM MÜLLER. *J. prakt. Chem.* 110, 1-9 (1925); cf. *C. A.* 19, 2193.—Reduction of 9,12-diphenyldiphenysuccinda-9,11-diene (I) with Zn dust in AcOH gives 9,12-diphenyl-10-diphenysuccindene (II), which gives a strongly fluorescing CHCl<sub>3</sub> soln. II adds Br in CS<sub>2</sub> but immediately splits off HBr (complete in 1-2 days) to give I. Reduction of I with AmOH and Na gives 9,12-diphenyldiphenysuccindane, which exists in 2 forms, m. 207-8° (III) and 166-7°; reduction of I or II with Pd and H<sub>2</sub> in AcOH gives III. Oxidation of II with CrO<sub>3</sub> (12 atoms O) gives 67% *o*-BrC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H; 6 atoms O gives a mixt. of *o*-BrC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H and (*o*-BrC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CO<sub>2</sub>H. 9,12-Di-[*p*-tolyl]-10-diphenysuccindene (IV), m. 200°; it behaves toward Br like II. 9,12-Di-[*p*-tolyl]diphenysuccindane (V), m. 188-9° and 145-6°; the higher melting isomer also results by reduction with Pd and H<sub>2</sub>. The *m*-deriv. corresponding to IV m. 179-80°; to V, m. 150°. X. Colored phenolic ethers of the diphenysuccindene series. K. BRAND AND WILLI KREY. *Ibid.* 10-25.—Diphenysuccindane-9,12-dione and *o*-C<sub>6</sub>H<sub>4</sub>(OC<sub>6</sub>H<sub>4</sub>)MgBr give 70-90% of 9,12-di-[*o*-phenetyl]diphenysuccindane-9,12-diol (VI), m. 213-5°; the corresponding *p*-deriv. (VII), pale yellow, m. 208°, results in 80-90% yields. VI, boiled with HCO<sub>2</sub>H or AcOH in AcOEt, yields 9,12-di-[*o*-phenetyl]diphenysuccinda-9,11-diene (VIII), reddish brown, m. 204-5°; the *p*-deriv. (IX), red-brown, m. 223-4°. VIII and CrO<sub>3</sub> in AcOH give *o,o'*-di-[*o*-ethoxybenzoyl]benzil, yellow, m. 244-5°, sol in cold concd. H<sub>2</sub>SO<sub>4</sub> with a brown color but decompd. by hot EtOH-KOH. It could not be condensed with *o*-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>. Further oxidation with H<sub>2</sub>O<sub>2</sub> in C<sub>6</sub>H<sub>5</sub>N gives *o*-[*o*-ethoxybenzoyl]benzoic acid, m. 161-3°. IX and CrO<sub>3</sub> give *o,o'*-di-[*o*-ethoxybenzoyl]benzil (X), golden yellow, m. 215-6°; increasing the amt. of CrO<sub>3</sub> or the use of an excess of KMnO<sub>4</sub> does not change the result. Ca(MnO<sub>4</sub>)<sub>2</sub> gives traces of *o*-C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)<sub>2</sub>. *o*-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> gives the quinoxaline, m. 227.5°, which, heated with NH<sub>4</sub>OH-HCl, EtOH and AcOH in a sealed tube for 10 hrs. at 140-50°, gives a small amt. of a compd., decomp. 170-80° and m. 202-3°. H<sub>2</sub>O<sub>2</sub> in C<sub>6</sub>H<sub>5</sub>N and X give *p*-EtOC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H-*o*, m. 135-6°. Reduction of VIII with activated Al in moist Et<sub>2</sub>O gives 9,12-di-[*o*-phenetyl]-10-diphenysuccindene, m. 250°, while AmOH and Na give 9,12-di-[*o*-phenetyl]diphenysuccindane, m. 175-6°. IX gives the corresponding *p*-series, m. 280-1° and 240-1°. 9,12-Di-[*o*-anisyl]-10-diphenysuccindene, m. 234-5°; the *p*-deriv. m. 244-45°. 9,12-Di-[*o*-anisyl]diphenysuccindane, yellow, m. 250-1°. The corresponding *p*-deriv. could not be obtained cryst. XI. Colored hydrocarbons of the diphenysuccindene series. An abnormal course of the Grignard reaction. K. BRAND, HEINZ LUDWIG AND L. W. BERLIN. *Ibid.* 25-36.—Diphenysuccindanedione and *o*-MeC<sub>6</sub>H<sub>4</sub>MgBr give a thick oil which, decompd. with EtOH, gave only the dione. With HCO<sub>2</sub>H or AcOH contg. a trace of H<sub>2</sub>SO<sub>4</sub> there results 9,12-di-[*o*-tolyl]diphenysuccinda-9,11-diene, brown, m. 240°. CrO<sub>3</sub> in AcOH at room temp. gives *o,o'*-di-[*o*-tolyl]benzil, yellow, m. 154°, while in boiling AcOH there results *o*-[*o*-tolyl]benzoic acid, crystg. with 1 H<sub>2</sub>O and m. in its H<sub>2</sub>O at 84°. *m*-MeC<sub>6</sub>H<sub>4</sub>MgBr behaves normally and yields 9,12-di-[*m*-tolyl]diphenysuccindane-9,12-diol, pale yellow, m. 150°; with HCO<sub>2</sub>H this yields the 9,11-diene, brown, m. 184-5°, which is oxidized by CrO<sub>3</sub> to *o,o'*-di-[*m*-tolyl]benzil, yellow, m. 159° and *o*-[*m*-tolyl]benzoic acid, crystg. with 1 H<sub>2</sub>O and m. 162°. 9,12-Di-[3,4-xylyl]diphenysuccindane-9,12-diol, m. 232°; the 9,11-diene, brown, m. 212°. *o*-MeC<sub>6</sub>H<sub>4</sub>MgBr and *O*-C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub> give 9,10-dihydroxy-9,10-di-[*o*-tolyl]-9,10-dihydroanthracene, m. 285° (decompn.); the C<sub>6</sub>H<sub>5</sub> and AcOH solns. show splendid fluorescence. The corresponding 2,4-xylyl deriv. m. 331-2° (decompn.); its solns. showed strong fluorescence; concd. H<sub>2</sub>SO<sub>4</sub> gives a bluish green color. The 2,5-xylyl deriv., m. 260° (decompn.); H<sub>2</sub>SO<sub>4</sub> gives a deep green color.

C. J. WEST

The mechanism of substitution reactions in the aromatic nucleus. II. EDWARD DE BARRY BARNETT, J. W. COOK AND M. A. MATTHEWS. *Rec. trav. chim.* 44, 217-23 (1925).—In previous papers (B., *et al.*, *C. A.* 18, 1237; 19, 59, 1251) it was argued that in many instances substitution in the aromatic nucleus probably consists primarily in addn. to a "bridge" bond, followed at once by reestablishment of the bridge by loss of H<sub>2</sub>O or halogen acid. Results already obtained with 1-chloro-, 1,3- and 1,8-dichloroanthracene rendered a closer study of anthracene dibromide (I) desirable. I may exist in 2 forms, viz., *cis* (II) and *trans* (III). Since on thermal decompn. I loses HBr mainly

giving 9-bromoanthracene (IV) it must have the *trans*-structure but the simultaneous production of anthracene indicates the presence of the *cis*-isomer or a tendency for a



change in configuration to occur. Instability and insoly. prevent the possible sepn. of I, II and III. Since I loses HBr easily even on keeping it at room temp it would be expected that this reaction would be promoted by the presence of a basic compd. This was not found to be true. Although  $\text{C}_6\text{H}_5\text{N}$  gives a dipyridinium salt the other bases behave differently. When I is kept for 24 hrs. at room temp. in contact with  $\text{Et}_3\text{N}$  and  $\text{Pr}_3\text{N}$  95% of I used is recovered unchanged and 5% is converted into IV. With  $\text{PhNMe}_2$  I reacts readily and although a quaternary salt is first formed the products isolated were 9-dimethylaminophenylantracene (V), green yellow, m.  $258^\circ$ , and 9,10-tetramethyldiaminodiphenyl-9,10-dihydroanthracene (VI), m.  $265^\circ$ .  $\text{Et}_3\text{NH}$  acting upon I causes loss of both HBr and Br, and the product is a mixt. of anthracene and IV while with piperidine I gives N-anthranylpiperidine. Primary and secondary amines act similarly and give  $\text{C}_6\text{H}_4\text{NNR}_2$  ( $\text{R} = \text{H}$  or alkyl) obtained by Padova (C. A. 3, 2678) and by B. and C. (C. A. 15, 2869) by heating 9,10-dihydroanthraquinyl 9,10-dipyridinium dibromide with  $\text{RNH}_2$  and  $\text{R}_2\text{NH}$  although they were at that time confused with the corresponding dihydroanthracene derivs. I with  $\text{NH}_3$  and  $\text{KOH}$  gave tars but small amts. of IV were isolated. With  $\text{Na}_2\text{S}$  anthracene was the main product and some dianthrone (VII). With  $\text{SO}_2$  HBr was lost easily and a 50% yield of IV was recovered. Attempts were made to replace the Br in I with OH in order to elucidate its geometrical configuration. I with moist  $\text{Ag}_2\text{O}$  gave a trace of VII but mostly anthracene (VIII) and anthraquinone (IX); dry  $\text{Ag}_2\text{O}$  in  $\text{PhMe}$  suspension gave the same result but more VII. When sapond. with  $\text{H}_2\text{O}$  or  $\text{H}_2\text{O-Me}_2\text{CO}$  with or without  $\text{CaCO}_3$  VIII, IX, VII and a 4th product that may prove to be the *cis*-HO compd. (X) sought were obtained. I with  $\text{NaOAc}$  gave resinous products from which a little IV was isolated. With anhydrous  $\text{EtOH}$  I gave a mixt. of VII and anthranol Et ether, which is an argument in favor of the *trans*-structure since *cis*-diethoxydihydroanthracene is probably stable enough to be isolated. It is hard to reconcile these facts with a static formula for I and it is concluded that change in configuration takes place. Attention is called to the work of Schroeter (C. A. 19, 1271) on the hydrogenation of VIII in which migration of H from the *meso*-positions to the  $\text{C}_6\text{H}_5$  rings occurred. E. J. W.

**1,5-Dichloroanthrone.** EDWARD DE BARRY BARNETT, J. W. COOK AND M. A. MATTHEWS. *Ber.* 58B, 976-83(1925).—The present study of various derivs. of 1,5-dichloroanthrone (I) furnishes an excellent illustration of the influence which halogen atoms on the ring exert on the reactivity of the *meso*-position in the anthracene nucleus. 1,5-Dichloroanthracene (II), like anthracene itself, is very resistant towards  $\text{H}_2\text{O}_2$ . With Br in boiling  $\text{AcOH}$  it gives its dibromide, but in the presence of  $\text{NaOAc}$  it forms a mixt. of 1,5-dichloroanthronyl acetate,  $\text{CO}(\text{C}_6\text{H}_4\text{Cl})_2\text{CHOAc}$  (III) and 1,5-dichloro-*cis*-9,10-dihydroanthrahydroquinol diacetate,  $\text{AcOCH}(\text{C}_6\text{H}_4\text{Cl})_2\text{CHOAc}$  (IV), also obtained from II with  $\text{Ph}(\text{OAc})_2$ , or by acetylation of 1,5-dichloro-*cis*-9,10-dihydroanthrahydroquinol; as it regenerates the latter on hydrolysis, there is no change in the geometrical configuration in this reaction, while the hydrolysis of the corresponding dichloride is accompanied by a partial transformation into the *trans*-isomer. 1,2,5-dichloroanthranol acetate (V) and 1,5-dichloroanthranol Me ether (VI) on bromination all give 1,5-dichloro-9-bromoanthrone (VII), while anthranol Me ether (VIII) gives 9-bromoanthranol Me ether. This difference in behavior is explained by the fact that in addn. to the anthracene "bridge" the tendency to form *trans*-compds. predominates, while the influence of the halogen atoms in II finds expression in the formation of *cis*-compds. In the former case, therefore, splitting off of HBr results in a restoration of the "bridge" while in the latter

the greater stability of the *cis*-structure permits only hydrolysis of the *gem*-bromohydrin group as the chief reaction. In the acetates, it is the very unstable character of the bromoacetoxy groups which in both cases brings about the latter type of reaction. Nitration also in both cases results only in splitting off of the Me group. Similarly, in VIII it is the very unstable nature of the semiacetal group in the addn. product,  $\text{MeOC}(\text{OH})(\text{C}_6\text{H}_4)_2\text{CHNO}_2$ , which must be formed first in the reaction, which is responsible for the demethylation occurring more readily than the restoration of the "bridge." Again, while 9-bromoanthrone is exceedingly reactive and decomps on standing at room temp., VII can be recovered almost unchanged after boiling 10 min. in xylene, although on longer boiling it loses Br and forms 1,5,1',5'-tetrachlorodianthrone. Short boiling with dil. alkali also does not attack VII, nor does 3 hrs. treatment with dry  $\text{NH}_3$  in boiling  $\text{C}_6\text{H}_6$  suspension. On hydrolysis with aq.  $\text{Me}_2\text{CO}$  it gives 1,5-dichloro-9-hydroxyanthrone (IX), whose OH group can easily be replaced by Cl by treatment with HCl, the resulting 1,5,9-trichloroanthrone (X) is quite stable, while 9-chloroanthrone cannot be prepd at all. The acetate (III) of IX is easily obtained from VII with NaOAc. On acetylation, best in  $\text{C}_6\text{H}_5\text{N}$ , both III and IX yield 1,5-dichloroanthranthraquinone diacetate (XI) (Eckert and Pollak (C. A. 11, 2772), describe under this name a compd., m. 249°, which they claim to have obtained by reduction of 1,5-dichloroanthraquinone (XII) with Al powder in concd.  $\text{H}_2\text{SO}_4$  in the presence of  $\text{Ac}_2\text{O}$ , but a repetition of their work gave a substance, m. 312°; their product was probably unchanged XII, which m. 250°). While 9-bromoanthrone with org. bases yields almost without exception dianthrone, 9-bromodianthrone and dianthraquinone, in the case of VII there is generally a replacement of the Br atom. With  $\text{MeNH}_2$ , to be sure, small amts of 1,5,1',5'-tetrachlorodianthrone are also formed. With  $\text{C}_6\text{H}_5\text{N}$ , 9-bromoanthrone forms a salt and VII undergoes the same reaction to a small extent but under the usual exptl. condition the  $\text{C}_6\text{H}_5\text{N}$  ring is ruptured and the salt cannot be isolated; the product is a very deeply colored substance which could not be purified and forms no  $\text{C}_6\text{H}_5\text{N}$  salt when boiled with HCl. By treating the VII with  $\text{C}_6\text{H}_5\text{N}$  in the presence of  $\text{Ac}_2\text{O}$ , however, the formation of the colored product can be avoided and there is obtained in good yield

1,5-dichloroanthranthyl acetate-9-pyridinium bromide,  $\text{ClC}_6\text{H}_3\begin{matrix} \text{C(OAc)} \\ \text{C(NBrC}_5\text{H}_5\text{)} \end{matrix}\text{C}_6\text{H}_4\text{Cl}$  (XIII), which is hydrolyzed by HBr to 1,5-dichloro-9-hydroxyanthranthylpyridinium bromide (XIV), or its ketonic isomer, 1,5-dichloroanthranthylpyridinium bromide; this is not very stable and is easily converted by dil. alkalis into a deeply colored substance which differs from that obtained from VII and  $\text{C}_6\text{H}_5\text{N}$  in the absence of  $\text{Ac}_2\text{O}$  in that on boiling with HCl it forms a  $\text{C}_6\text{H}_5\text{N}$  salt. V (10.3 g. from 10 g. I and  $\text{Ac}_2\text{O}$  in  $\text{C}_6\text{H}_5\text{N}$  on the  $\text{H}_2\text{O}$  bath), straw-yellow, m. 178°. VI (9.1 g. from 10 g. I with  $p\text{-MeC}_6\text{H}_4\text{SO}_3\text{Me}$  and NaOH in boiling alc.), m. 104°. Et ether (10 g. from 10 g. I), yellow, m. 103°. These ethers, boiled 2-4 hrs. in AcOH contg. a little  $\text{H}_2\text{SO}_4$  or HCl, are completely dealkylated with formation of L. VII, almost colorless, m. 214° (decomps.). X, m. 194-5°, hardly attacked by boiling dil. aq. NaOH. 1,5-Dichloro-9-nitroanthrone, from I, V or VI in AcOH with concd.  $\text{HNO}_3$ , m. 168° (decomps.), only very slightly sol. in boiling NaOH. 1,5-Dichloroanthranthyl Et ether, from VII and boiling alc., m. 159°. III, light yellow, m. 178°. IV, light yellow, darkens 200°, m. 314°. 1,5-Dichloro-9-dimethylaminoanthrone, from VII and dry  $\text{MeNH}_2$  in boiling  $\text{C}_6\text{H}_6$ , m. 195°, sol. in dil. HCl. The 9-NEts and 9-piperidino analogs were similarly prepd. 9-PkNH compd., yellow, m. 193°. 9- $p\text{-Me}_2\text{NC}_6\text{H}_4$  deriv., yellow, m. 277°. XIII, yellow, leaflets with 0.5 H<sub>2</sub>O, m. 230° (decomps.), gives in  $\text{H}_2\text{O}$  a red ppt. with  $\text{NiCl}_2\text{OH}$ , NaOH or  $\text{Na}_2\text{CO}_3$ . XIV, begins to decomp. 150°, m. completely 250°. C. A. R.

Polyhydroxy- and polyhydroxymethylanthraquinones. VI. Syntheses from opianic acid and phenols or cresols. R. A. JACOBSON AND ROGER ADAMS. J. Am. Chem. Soc. 47, 2011-8(1925); cf. C. A. 19, 632.—Equimol. quantities of opianic acid and the phenol are intimately mixed and  $\text{H}_2\text{SO}_4$  of the proper strength slowly added in the ratio of 65 cc. acid for 25 g. acid; for simple cresols, 75% acid is used, for the Br derivs., 85%. The yields of pure product are 50-70%. The following 2-derivs. of 3,6-dimethoxyphthalide were thus prepd.: from  $p\text{-MeC}_6\text{H}_4\text{OH}$ , 2-hydroxy-3-methylphenyl (I), m. 181.5-3°; from 1,3,4- $\text{Me}_3\text{(HO)C}_6\text{H}_3$ , 2-hydroxy-3,5-dimethylphenyl, m. 170-1°, from  $p\text{-O}_2\text{NC}_6\text{H}_4\text{OH}$ , 2-hydroxy-5-nitrophenyl, m. 269-70°; from  $o\text{-(MeO)-C}_6\text{H}_4$ , 3,4-dimethoxyphenyl (II), m. 122-3°; from  $o\text{-HO-C}_6\text{H}_4\text{OMe}$ , 3-methoxy-4-hydroxyphenyl (III), m. 171-2°; from  $o\text{-MeC}_6\text{H}_4\text{OH}$ , 3-methyl-4-hydroxyphenyl (IV), m. 185-6°; from 3,4- $\text{Me}_2\text{BrC}_6\text{H}_3\text{OH}$ , 2-hydroxy-4-methyl-5-bromophenyl (V), m. 180-1°, and 2-hydroxy-5-bromo-6-methylphenyl (VI), sinters 265°, m. 270-1°; from 4,6,3- $\text{BrMeC}_6\text{H}_3\text{OH}$ , 2-hydroxy-3,5-dibromo-6-methylphenyl (VII), m. 205-55°. Reduction of these

products with Zn dust and 10% NaOH by boiling for approx. 15 hrs. gives the following 2-derivs. of 5,6-dimethoxybenzoic acid: I, 2-hydroxy-5-methylbenzyl, 79% yield; II, 3,4-dimethoxybenzyl, 71%; III, 3-methoxy-4-hydroxybenzyl, 79%; IV, 3-methyl-4-hydroxybenzyl, 76%, thick sirup; V, 2-hydroxy-4-methylbenzyl, 83%, thick sirup; VI or VII, 2-hydroxy-6-methylbenzyl, 63 or 82%. The sirupy acids are sufficiently pure for conversion into anthrones by allowing them to stand with 85% or concd  $\text{H}_2\text{SO}_4$  until soln. is complete, there were thus obtained the following 9,10-dihydroxy-9-ketoanthracenes: 1,2,6,7-tetramethoxy, yellow, m 153-4°, 80% yield; 1,2,6-trimethoxy-7-hydroxy, 95%; 1,2-dimethoxy-6-methyl-7-hydroxy, 52%, 1,2-dimethoxy-5-hydroxy-7-methyl, 14%, 1,2-dimethoxy-5-hydroxy-8-methyl, 95% (Ac deriv, greenish yellow, m 188.5-9°. Oxidation of the anthrones with  $\text{CrO}_3$  in AcOH (mol ratio, 1.133) gives the corresponding anthraquinones: 1,2-dimethoxy-5-hydroxy-8-methyl, m 168-9°, 42% yield, 1,2-dimethoxy-5-acetoxy-8-methyl, m. 173-1°, 1,2-dimethoxy-5-hydroxy-7-methyl, m 231.5-2.5°, 28%; 1,2,6-trimethoxy-7-hydroxy, m 269-70°, 55%. 1,2-dimethoxy-6-methyl-7-hydroxy, m. about 310°, 55%, and 1,2,6,7-tetramethoxy, m 244-5°, 85%. These products were demethylated by HBr in AcOH, giving the following anthraquinones: 1,2,5-trihydroxy-8-methyl, red, decomps 290°, 85% yield, tri-Ac deriv, light yellow, m 204-5°; 1,2,6,7-tetrahydroxy, orange, m above 330°, 69%, tetra-Ac deriv, light yellow, m 239-41°; 1,2,7-trihydroxy-6-methyl, orange-red, m above 330°, 70%, tri-Ac deriv., light yellow, m. 232-3°.

C. J. WEST

Dyes derived from phenanthraquinone. VI. Phenanthraquinonephenylazomethines and phenanthraphenazine dyes. ANUKUL CHANDRA SIRCAR AND BENOV KUMAR SEN GUPTA. *Quart J. Indian Chem. Soc.* 1, 321-8 (1925), cf. C. A. 19, 2208.—2,7-Diaminophenanthraphenazine (I), diazotized in the usual way and coupled with  $\beta\text{-C}_6\text{H}_4\text{OH}$ , gives phenanthraphenazine-2,7-bis-[1'-azo-2'-naphthol], does not m. 300°, gives a reddish violet soln. in concd  $\text{H}_2\text{SO}_4$ , dyes wool reddish violet from an acid bath and cotton a pink from a neutral bath. The corresponding 1'-azo-2'-hydroxy-3'-naphthoic acid, dyes wool violet from an acid bath and cotton light violet from a neutral bath. I and  $p\text{-Me}_2\text{NCH}_2\text{CHO}$  in HCl, followed by liberation of the base with  $\text{NH}_3$ , give 2-aminophenanthraquinone-7-[1'-azomethine-4'-dimethylaminobenzene], blue-black needles, does not m 300°, concd  $\text{H}_2\text{SO}_4$  gives a yellowish brown color; wool is dyed bottle-green from an AcOH bath. The corresponding 1'-azomethine 2',4'-dihydroxybenzene forms black needles. The 5 following phenanthraquinone-2,7-bis derivs., were prepd. similarly: 1'-azomethinebenzene, violet, from BzH; 1'-azomethine-4'-methylbenzene, brilliant needles with Cu luster, from  $p\text{-MeC}_6\text{H}_4\text{CHO}$ ; azocinnamylidinemethine, violet, from  $\text{PhCH:CHCHO}$ ; 1'-azomethine-4'-methoxybenzene, reddish violet, from  $p\text{-MeOC}_6\text{H}_4\text{CHO}$ ; 1'-azomethine-2'-hydroxybenzene, brilliant scarlet, from  $o\text{-HOC}_6\text{H}_4\text{CHO}$ . 2-Acetylaminophenanthraquinone-7-[1'-azomethine 2'-hydroxybenzene,] violet, sol. in concd.  $\text{H}_2\text{SO}_4$  with a blood red color, dyes wool violet shades from an AcOH bath; this results in AcOH; in EtOH the free amino deriv forms crystals with 1 EtOH, reddish violet. Phenanthraquinone-4-[1'-azomethine-3'-nitrobenzene], orange-red, dyeing wool chocolate shades from an AcOH bath; the corresponding 2-deriv., is brownish black. 4-Aminophenanthraquinone-5-[1'-azomethine-3'-nitrobenzene], amorphous violet powder; the corresponding 2-aminophenanthraquinone 7-[1'-azomethine-3'-nitrobenzene], violet needles.

C. J. WEST

Structure of the humic acids and coals. J. MARCUSSEN. *Ber.* 58B, 869-72 (1925).—Furan, fural and furancarboxylic acid with concd HCl yield a humin insol. in solvents, which on gentle fusion with alkalis is converted into humic acids, and M. had suggested, on the basis of these syntheses, that the humic acids contain a furan nucleus. Eller objected, however, that in nature it is the humic acids which are formed first and then the humins (C. A. 15, 2632). M. has now found that fural can be converted directly into humic acids by auto-oxidation; freshly distd. fural in 1% NaOH is spread on cotton and exposed to O under a bell jar; it at once becomes brown and the color gradually becomes deeper and deeper. The cotton is now treated with  $\text{H}_2\text{O}$ , the aq. alk. soln. freed from unchanged fural with  $\text{Et}_2\text{O}$ , warmed a short time to remove the  $\text{Et}_2\text{O}$  and acidified. The pptd. humic acid is readily sol. in NaOH and  $\text{NH}_4\text{OH}$ . The conditions under which it is formed are so mild that it is not necessary to assume an intermediate rupture of the ring. Probably 3 furan nuclei condense to a 6-membered ring system (see figure), a structure which would explain many of the reactions of the humic acids which have been advanced as arguments in favor of their purely aromatic character. Fischer and Schrader state that on pressure oxidation sugar-humic acids yield benzene- and furancarboxylic acids while natural humic acids give only  $\text{C}_6\text{H}_6$  derivs. They tested for the furan derivs. by means of the pine-splinter reaction after splitting

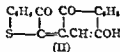
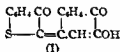


off  $\text{CO}_2$  and with the natural humic acids got a crimson instead of a green color. The natural humic acids, however, unlike those obtained from sugar, always contain N which, at the high temp. of the reaction, yields with furan the basic pyrrole which with a pine splinter gives a characteristic crimson color, so that F.'s and S.'s observation really supports the assumption of the presence of furan nuclei in the natural humic acids. When Wellmitzer coal, which consists mostly of free humic acids, is subjected to dry distn. and the evolved gas is passed into alc. HCl, the alc. soln. on addn. of concd aq. HCl and evapn., yields black, alkali-insol. condensation products; the distillate on evapn. gives a yellow brown oil yielding alkali sol. humic acids on heating to dryness with HCl, and the aq. soln. of the oil reddens fuchsin- $\text{SO}_2$ , reduces cold  $\text{NH}_3\text{-AgNO}_3$  and gives the  $\text{PhNH}_2$ ,  $\text{HIOAc}$  reaction of furan aldehydes. Similar results were obtained with the Et humates prepd. from the coal with 3% alc. HCl, as also with lignic acids (prepd. from wood with NaOH under pressure) and with Na ligninsulfonate, showing that lignin likewise contains furan nuclei. The process whereby natural humic acids gradually change into peat can be imitated in the lab. by heating the acids at  $250^\circ$  in the absence of air (e. g., in mineral oil); there are thus formed pyrohumic anhydride and humic ketones, which are constituents of peat. In nature, the change occurs at a lower temp. and the furan nucleus is not ruptured; in (fresh) coke liquor of an ordinary peat, furan aldehydes can be detected by color reactions and humic acids can be obtained by treatment with concd. HCl. The natural transformation of peat into anthracite can also be imitated in the lab. by heating under pressure; the furan nucleus is not ruptured and both peat and anthracite show the same behavior towards concd.  $\text{H}_2\text{SO}_4$ , fuming  $\text{HNO}_3$ ,  $\text{ICl}$ ,  $\text{HCl}$  in  $\text{Et}_2\text{O}$ , etc.; dry distn. of anthracite yields benzofuran (up to 40% of the 155-85° fraction of the tar). C. A. R.

Magnesylypyrrole and its use in the synthesis of pyrrole compounds. B. Onop Mem. acad. Lincei [v] 14, 510-623 (1923).—The vol. of  $\text{C}_4\text{H}_5$ , developed in the reaction between magnesylythane and the magnesyl derivs. of tripyrrole and tri-indole proves that each of these compds. contains only 1 secondary N atom. Magnesylyndole forms, with pyridine and quinoline, compds. similar to those given by magnesylypyrrole (A. H. accad. Lincei 13, ii, 100-6 (1904); 16, i, 413-8, 538 (1907); C. A. 5, 686). Magnesylycarbazole gives a definite compd. with 1 mol. of ether. S converts magnesylyndole and magnesyly-2-methylindole into cryst. compds., diindolyl sulfide and  $\alpha, \alpha'$ -dimethylindolyl sulfide, resp.; liquid  $\text{SO}_2$  converts the former into diindolyl sulfoxide (cf. Angeli and Peroni, C. A. 13, 3324; 14, 172). 3-Ethylindole, b.  $276-7^\circ$  (picrate, m.  $144.5^\circ$ ), is obtained in the same way as 3-methylindole (C. A. 5, 2638). 1-Methylindole and 1,3-dimethylindole, b.  $225-32^\circ$  (picrate, m.  $140^\circ$ ), are also obtained similarly to 3-methylindole by shortening the period of heating. Phyllopyrrole is synthesized in small yield by the action of MeI on the magnesyl deriv. of 2,5-dimethyl-3-ethylpyrrole, but the principal product of this reaction is a pyrrolenine. 2-Benzyl pyrrol ketone, b.  $335-40^\circ$  (partial decompn.), m.  $95^\circ$  (phenylhydrazone, m.  $133^\circ$ , and Ag deriv. described), is prepd. by the action of  $\text{PhCH}_2\text{COCl}$  on magnesylypyrrole. The following are obtained similarly: 2,3,5-trimethyl-3-benzoylpyrrole, m.  $172-3^\circ$  (cf. C. A. 4, 2460); 4-[6-methoxyquinolyl] 2 pyrrol ketone, m.  $139^\circ$ ; 4-[6-methoxyquinolyl]-2-[3,5-dimethylpyrrol] ketone, m.  $165^\circ$  (cf. Karrer, C. A. 12, 1290); 2-methyl-3-chloroacetylindole, m.  $201^\circ$ ; acetylcarbazole, m.  $70^\circ$ ; propionylcarbazole, m.  $90^\circ$  (alc. KOH gives carbazole and  $\text{PhCO}_2\text{H}$ ; picrate, m.  $140^\circ$ ;  $\text{HNO}_3$  gives nitropropionylcarbazole, m.  $233^\circ$ ); benzoylcarbazole, m.  $98^\circ$  [boiling aq. alkali gives carbazole and  $\text{BrOH}$  (cf. C. A. 5, 2638)];  $\text{COCl}_2$  converts magnesylypyrrole into 2,2-dipyrrol ketone, m.  $160-1^\circ$  (Ag deriv. described), which is also obtained by the action of pyrrole-2-carboxylic chloride on magnesylypyrrole.  $\text{EtNO}_2$  reacts with magnesyly-2-methylindole to give a very small yield of 3-nitro-2-methylindole. At  $260^\circ \text{CO}_2$  and magnesylypyrrole give pyrrole-3-carboxylic acid m.  $161^\circ$  (cf. C. A. 5, 680). In the absence of solvent at high temp., magnesylycarbazole and  $\text{CO}_2$  give carbazolecarboxylic acid, m.  $275-6^\circ$ , with slight blackening; Ag and Ba derivs. are described (cf. C. A. 5, 2638; 6, 2234). The action of  $\text{ClCO}_2\text{Et}$  on magnesylyscatole at  $140^\circ$  gives only Et 3-methylindole-1-carboxylate, but at  $250^\circ$  a small yield of Et 3-methylindole-2-carboxylate, m.  $134^\circ$ , is obtained. By the action of the appropriate  $\text{ClCO}_2\text{H}$  ester on magnesylypyrrole the following are obtained, usually in 85-90% yield: Me pyrrole-2-carboxylate, m.  $73^\circ$  ( $\text{NH}_3$  gives the amide, m.  $176^\circ$ ); Me pyrrole-1,2-dicarboxylate, m.  $141^\circ$ ; Et pyrrole-1-carboxylate, b.  $235^\circ$ , m.  $38^\circ$ ; N-Pr pyrrole-2-carboxylate, b.  $161-5^\circ$ ; isopyrrole-2-carboxylate, b.  $119-22^\circ$ ; isopyrrole-2-carboxylate, b.  $156-90^\circ$ . Et indole-2-carboxylate, m.  $107^\circ$ ; Et 3-methylindole-1-carboxylate and Et 2-methylindole-3-carboxylate, m.  $135^\circ$ , are obtained by the action of  $\text{ClCO}_2\text{Et}$  on the magnesyl derivs. of indole, scatole and 2-methylindole, resp. In this way magnesylycarbazole gives Et diphenylcarbamate, m.  $77.5^\circ$ . Besides 3,3'-diindyl (Ag

deriv.; osazone, m. 158°; quinoxaline, m. 163°), the action of  $(\text{COCl})_2$  on magnesylindole gives 2,2-diindyl, m. 273° (osazone, m. 170°, decompn., quinoxaline, m. 154°, decompn.), and 1,2-bisindyl, m. 320°.  $\text{CH}_3(\text{COCl})_2$  converts magnesylindole into diindylmethane, m. 287°. This substance is an equil. mixt. of keto and mono-enolic forms, the proportion of the former of which increases with rising temp. A Ag deriv. is described;  $\text{PhNHNH}_2$  gives 1-phenyl 3,5-diindylpyrazole, m. 236° (decompn.);  $\text{NH}_2\text{OH}$  gives 3,5-diindylisooxazole, m. 219° (decompn.); hydrolysis of the product from the action of semicarbazide results in 3,5-diindylpyrazole, m. 229° (decompn.), hydrolysis by alkali gives indole-3-carboxylic acid and 3-indolyl methyl ketone. Di-[2-methylindolyl]-methane, m. 219°, is obtained similarly from magnesyl-2-methylindole. In the same way as the preceding one, this compd. gives 1-phenyl 3,5-di-[2-methylindyl]pyrazole, m. 192° (decompn.); 3,5-di-[2-methylindyl]isooxazole, m. 174°; 3,5-di-[2-methylindyl]-pyrazole, m. 247° (decompn.) Diindylethane, m. 287° (Ag deriv. and dioxime m. 305°, decompn.), and di-[2-methylindolyl]ethane, m. 297° (decompn.) (dioxime, m. 267°), are obtained by the action of  $(\text{CH}_3\text{COCl})_2$  on magnesylindole and magnesyl-2-methylindole, resp. Et pyrrole-2-glyoxylate, m. 41.5° is obtained by the action of ethoxalyl chloride on magnesylpyrrole; it is readily hydrolyzed to the corresponding acid, m. 113° (decompn.). Et pyrrolacetate (C. A. 6, 3425) gives pyrrylphenylpyrazolone, m. 193°, and semicarbazone, m. 90°; alc.  $\text{NH}_3$  transforms it into the amide, m. 184°. The paper contains a full bibliographical record of previous work. B. C. A.

Indigo-like dyes of the naphthalene series. P. FRIEDLÄNDER *Ann.* 443, 211-23 (1925).—From the numerous patented dyes, F has selected the following as typical. 3-Hydroxy-1-naphthalene-2-thionaphthenindolignone (I), brown-violet, from  $\beta$ -naphthoquinone and hydroxythionaphthene by passing air through a slightly alk. EtOH soln. Ac deriv., brown-red.  $\text{PhNH}_2$  in AcOH gives the compd.  $\text{C}_{24}\text{H}_{19}\text{O}_2\text{NS}$ , dark blue,  $\alpha\text{-H}_2\text{NC}_6\text{H}_4\text{CO}_2\text{Me}$ , the compd.  $\text{C}_{24}\text{H}_{19}\text{O}_2\text{NS}$ , blue; with both these dyes, alk.  $\text{Na}_2\text{S}_2\text{O}_4$  gives a yellow bath which dyes cotton and wool blue.  $\alpha\text{-H}_2\text{NC}_6\text{H}_4\text{CO}_2\text{H}$  gives the dye  $\text{C}_{24}\text{H}_{19}\text{O}_2\text{NS}$ ;  $\text{H}_2\text{NC}_6\text{H}_4\text{N}_2\text{Ph}$ , the dye  $\text{C}_{24}\text{H}_{19}\text{O}_2\text{N}_2\text{S}$ , sol. in  $\text{PhNO}_2$  with a pure green color. 4-Hydroxy-2-naphthalene-2-thionaphthenindigo (II), dark needles, sol. in  $\text{C}_6\text{H}_5\text{N}$  with a green color, changed to blue on diln. with  $\text{H}_2\text{O}$ . Heating Orange I and hydroxythionaphthene with borax gives the 4-amino deriv., dark blue, sol. in 60°  $\text{H}_2\text{SO}_4$ ; Ac deriv., dark violet; the absorption spectrum in  $\text{C}_6\text{H}_6$  shows a max. at 600  $\mu$ .  $\alpha$ -Naphthohydroquinol and  $\text{PhNH}_2$  give 4-phenylamino-1-naphthol (III), m. 80-90°; Na salt, glistening leaflets;  $\text{K}_3\text{Fe}(\text{CN})_6$  gives naphthoquinonanil. Me ether, m. 159°. 4-p-Chlorophenylamino-1-naphthol, m. 96°; Me ether, m. 125°. Phenylaminonaphthalenethionaphthenindigo, dark blue, from naphthoquinonanil and hydroxythionaphthene. Isatinanilide and III give good yields of phenylaminonaphthalene-2-indolindigo, blue; the p-Cl deriv. is less sol. than the unsubstituted deriv.

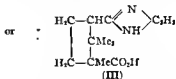
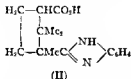


C. J. WEST

Synthesis of N-methylscatole. K. KEIMATSU AND M. INOUE. *J. Pharm. Soc. Japan*, No. 518, 351-4 (1925).—Using Rāth's method of synthesizing N-ethylindole (C. A. 18, 2898), K. and I. synthesized N-methylscatole using, however, chloroacetone acetal instead of chloroacetal. 21.4 g. (2 mols.)  $\text{PhNHMe}$  and 16.7 g. (1 mol.) chloroacetone acetal are heated at 250-60° for 6 hrs. in the sealed tube. After cooling, the content is washed with dil. HCl and subjected to steam distn. without neutralizing the acid. Unlike Rāth's reaction, the distn. can be done without making alk. The oil obtained (4 g.) b. 234-2°,  $d_4^{20}$  1.70-5°. The analysis of this oil does not correspond exactly to  $\text{C}_{10}\text{H}_{11}\text{N}$ , because of an impurity, but its picrate, m. 143-4°, shows the compn.  $\text{C}_{17}\text{H}_{11}\text{N} \cdot \text{C}_6\text{H}_5\text{N}_3\text{O}_7$ . From the mother liquid after distn., the expected intermediate product, N-methyl-3-methylethoxydihydroindole could not be isolated; instead K. and I. found  $\text{PhNHMe}$ . With chloroacetone and the  $\text{PhNHMe}$ , no reaction took place. S. T.

Color of complex diazoles. II. GOPAL CHANDRA CHAKRAVARTI AND INDUBHUSAN SEN GUPTA. *Quart. J. Indian Chem. Soc.* 1, 329-38 (1925); cf. C. A. 19, 830. In a further study of the relation between the color and constitution of the pyridine-iminazole systems, camphoric anhydride (I) was condensed with diamines; the diazoles thus prepd. were all colorless. I and  $\alpha\text{-C}_6\text{H}_4(\text{NH}_2)_2$ , heated in EtOH 4-5 hrs. give a mixt. of 3-phenyleneamidinetrimethylcyclopentanecarboxylic acids: (II), m. 233°, insol. in  $\text{Et}_2\text{O}$ ; (III), m. 203° and then at 242°; and (IV), m. 242°. III being less sol. in MeOH. The relation of III and IV may be that of camphoric and isocamphoric acids. The diazole

(V) from II, m 132°, that from III and IV, m. 138°; V crystals with 1.5 EtOH; when crystd from light petroleum, it m 95°. 1,3,4-MeC<sub>6</sub>H<sub>3</sub>(NH<sub>2</sub>)<sub>3</sub> likewise gave 3 *tolylene acids*, m 239-40°, 228-9° and 250-2°, the *diazoles* from the first and last m 93° and 97°, resp., and cryst with 3 EtOH. 1,2-C<sub>10</sub>H<sub>6</sub>(NH<sub>2</sub>)<sub>2</sub> gave 2 *naphthalene acids*, m. 180-2° and 235° (decompn), the *diazole* from the former m. 80-2°.



C. J. WEST

*α,β-Diphenyl-μ(m)-nitrophenylglyoxaline*; *α,β(p)-dinutrophenyl-μ(p)-nitrophenylglyoxaline* and several of its derivatives. J. TROGER AND H. THOMAS. *J. prakt. Chem.* 110, 42-63(1925); cf *Ibid* 64, 530(1901) — *α,β Diphenyl-μ(m)-nitrophenylglyoxaline(m-nitrolophine)* (I) results in 70-90% yields by heating 6.8 g m-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CHO, 10.4 g Bz<sub>2</sub> and 15-20 cc. 22-25% NH<sub>4</sub>OH 2 days at 180°; it is stable towards concd. HCl and 50% aq KOH, but warming with 50% EtOH-KOH decomps the glyoxaline ring, giving BzOH, m-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H and 2 mols NH<sub>3</sub>. Nitration of lophine by warming 5 g in 25-30 cc. HNO<sub>3</sub> (d. 1.4) while adding 35 cc HNO<sub>3</sub> (d. 1.51) gives *α,β di-p nitrophenyl μ(p)-nitrophenylglyoxaline(p-trinitrolophine)*, *IIN* C(C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>):N C(C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>).CC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>, yellow, m

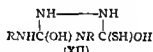
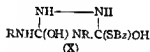
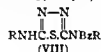
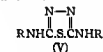
147°. It is not altered by heating 23 hrs with concd HCl at 240° but is decompd by 25% KOH. *m-Aminolophine* (II) results in 90% yields by reducing I with Zn dust. Definite products could not be obtained from the reduction of the tri-NO<sub>2</sub> deriv. Diazoizing I and heating the soln to 80-90° gives *m hydroxylophine*, m 182° (decompn.), whose Bz deriv, m 256°. The diazo compd. condenses with m-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub> to give *lophine m-azoresorcinol*, amorphous, red-brown product, m 222°, and with β-C<sub>10</sub>H<sub>7</sub>OH to give *lophine m-azo-β-naphthol*, blood red, m. 123°; the *α naphthol deriv.*, blood-red, m 194°. K μ-(m)-phenyl-α,β-diphenylglyoxalinediazosulfonate, needles, from the diazo soln and K<sub>2</sub>SO<sub>4</sub>, concd HCl splits off H<sub>2</sub>SO<sub>4</sub>. The Na salt was also prepd, while with satd H<sub>2</sub>SO<sub>4</sub> solns there results the *free acid*, yellowish white ppt.; this also results from the acid diazo soln and K<sub>2</sub>SO<sub>4</sub>. Passing SO<sub>2</sub> into the diazo soln. gives μ-(m)-phenyl-α,β-diphenylglyoxalinesulfonic acid, amorphous. MeI and II in MeOH give the compd C<sub>21</sub>H<sub>19</sub>N<sub>3</sub>, H<sub>2</sub>O (III), m 95°; 3 mols MeI and 3 mols KOH with 1 mol. II in MeOH give a compd C<sub>21</sub>H<sub>19</sub>N<sub>3</sub>, 3H<sub>2</sub>O, m 159-60°. III and AgCl give the corresponding Cl deriv, cryst with 1 H<sub>2</sub>O and m 249°; distg with H<sub>2</sub>O and a little H<sub>2</sub>SO<sub>4</sub>, splits off 1 Cl atom as HCl. III behaves similarly, but if FeCl<sub>3</sub> is added, both I are split off as HI. With 1 mol Ag<sub>2</sub>O, III gives a base, C<sub>21</sub>H<sub>19</sub>N<sub>3</sub>O<sub>2</sub> or C<sub>21</sub>H<sub>19</sub>N<sub>3</sub>O<sub>2</sub>, m 87°, whose chloroplatinate, Au yellow, contains 24.7% Pt. Heating with NaOH gives volatile basic compds. With an excess of Ag<sub>2</sub>O there also results a base, m 152-3°, whose Au-yellow chloroplatinate contains 25.08% Pt. II and PhClH<sub>2</sub>Cl give the compd. C<sub>21</sub>H<sub>19</sub>N<sub>3</sub>Cl<sub>2</sub>, m. 172°.

C. J. WEST

Condensation of the isomeric tolyl-2-thio-4-ketothiazolidines (rhodanic acids) with substituted vanillins. R M HANN. *J. Am. Chem. Soc.* 47, 1998-2002(1925).—The purpose of this study was to det. the effect of the relative position of the Me group in the PhMe residue, as well as the halogen substitution effect in such a series, upon their spectrochem behavior. Measurement of the absorption of these compds. in AcOH indicates that the max absorption occurs too far in the red end of the spectrum to allow use of direct absorption measurement methods. 5-Iodovanillin, m. 180°, monoclinic, *a b c* = 1.014.1 0.8161. β 87° 30'. It belongs to the buxial class, *a* 1.505, γ above 1.740, the optical sign is +, the sign of elongation — and the optic axial angle approx 22°. 5-Chlorovanillin, m 165°. The halogen vanillal tolylrhodanic acids are formed by the condensation of the isomeric tolylrhodanic acids with substituted vanillins in AcOH-AcONa. There were thus prepd the following 2-thiothiazolidines: 3-o-Tolyl-4-keto-5-[5 bromovanillal], iridescent, yellow-brown, m. 207° (slight decompn); the yield in all cases was quant. The 5-Cl deriv, brilliant yellow, m 196°; 5-I deriv, orange-red, m. 213°; 5-NO<sub>2</sub> deriv, golden brown, m 205° (decompn). 3-m-Tolyl-4-keto-5-vanillal, deep yellow, m 210°; 5-B deriv., light yellow, m. 201° and, after solidification, 223-4°; 5-Cl deriv, brilliant yellow, m 210°; 5-I deriv., yellow-brown, m 190-1° (decompn); 5-NO<sub>2</sub> deriv brown, m. 220° (decompn) 3-p-Tolyl-4-keto-5-[5-bromo-

ranillal], brilliant, light yellow, m. 223°, 5-Cl deriv., brilliant yellow, m. 221°; 5-I deriv., deep yellow, m. 243°, 5-NO<sub>2</sub> deriv., golden brown, m. 214–5° (decompn.). These products give brilliant red solns. in concd H<sub>2</sub>SO<sub>4</sub>. C. J. WEST

**Derivatives of di-*o*-tolylhydrazodithiocarboxamide.** EMIL FROMM AND PAUL SZENDRO *Ber* 58B, 970–5 (1925).—F and Soffer (C. A. 18, 378) had found that RNHCNHNH<sub>2</sub> (I) (R = *o*-MeC<sub>6</sub>H<sub>4</sub>) heated with a large excess of BzCl reacts according to the equation  $2I + 2BzCl = C_{15}H_{11}O_2N_2S$  (II) + H<sub>2</sub>S + 2HCl + NaI<sub>2</sub>, and with a smaller excess of BzCl according to the equation  $2I + BzCl = C_{15}H_{11}O_2N_2S$  (III) + H<sub>2</sub>S + N<sub>2</sub>H<sub>4</sub> + HCl. II, m. 252°, is derived from (RNHCNHNH-)<sub>2</sub> (IV), being the di-Bz deriv. of the diazole (V) resulting from IV by loss of H<sub>2</sub>S. III, m. 168°, splits off BzOH when heated with alc. alkalis, giving a compd. C<sub>15</sub>H<sub>11</sub>O<sub>2</sub>N<sub>2</sub>S (VI), m. 154°. F and Szendro have now succeeded in obtaining III from IV, not by heating it directly with BzCl but through an intermediate (hydrated) product formed by the action of BzCl and alkali on it, showing that III is also derived from IV and is formed from it by the loss of H<sub>2</sub>S. The only 2 compds. which can be formed from IV by loss of H<sub>2</sub>S are V and the triazole VII. When, however, V and VII are heated with BzCl, they both give II. The transformation of VII into V can most simply be explained by assuming that the ring is ruptured between the RNHC and NR groups and that the resulting RNHCCI NN C(NBzR)SII, formed by addn. of BzCl, then loses HCl and gives VIII, which at once reacts with another mol. of BzCl to form II. By the Schotten-Baumann method, however, while V again yields II, VII forms a compd. C<sub>15</sub>H<sub>11</sub>O<sub>2</sub>N<sub>2</sub>S (IX), m. 156°, also obtained from IV with BzCl and NaOH, which probably has the structure X or RNHCNHNHC(SBz)(NHR)OH, as it is the intermediate product in the formation of III from IV, III probably has the structure XI; with alc. alkalis, III loses the Bz residue but adds 2 mols. H<sub>2</sub>O and the resulting VI must be XII or RNHCNHNHC(SH)(NHR)OH. VI cannot be benzoylated by the Schotten-Baumann method but on heating with BzCl regenerates III. Attempts to establish the presence of a SH group in VI by means of PhCH<sub>2</sub>Cl and NaOH led to the formation of a compd. C<sub>22</sub>H<sub>23</sub>N<sub>2</sub>S, m. 112°, which possibly has the structure PhCH<sub>2</sub>NHN C(SCH<sub>2</sub>Ph)NHR.



4-*o*-Tolyl-5-*o*-toluidino-1,2,4-triazole-3-disulfide, from VII in boiling alc. suspension with alc. I, or in aq. suspension with excess of Br water, m. 168°, mol. wt. in freezing C<sub>10</sub>H<sub>8</sub> 609, regenerates VII on heating with aq. alkali and neutralizing with dil. HCl.

C. A. R.

**The oxidation of arylazo- $\beta$ -naphthylamine in acetic acid solution with hydrogen peroxide.** G. CHARRIER AND G. B. CRIVIA *Gazz. chim. Ital.* 55, 11–28 (1925).—The study of the oxidation of *o*-aminoazo compds. with H<sub>2</sub>O<sub>2</sub> in AcOH was extended to arylazo- $\beta$ -naphthylamines (I) (C. A. 18, 265). Other compds. are formed besides the 2-*N*-aryl- $\alpha,\beta$ -naphthotriazole oxides (II). II may exist in 3 isomeric forms (III, IV and V) and the derivation of these from I, according to the views of Angeli, is represented



schematically. It is not known to which series the II described here belong. Since isomers III and V might be obtained by reduction of the unknown *o*-nitroazo compds. 1,2- and 2,1-PhN NC<sub>10</sub>H<sub>7</sub>NO<sub>2</sub>, resp. C and C. attempted without success to prep. them from the corresponding *o*-nitronaphthylamines and PhNO. In the action of H<sub>2</sub>O<sub>2</sub> + AcOH on I, 2 main reactions take place independently at 60–100°, while the velocity of the 1st is greater at low temps.: I + H<sub>2</sub>O<sub>2</sub>  $\rightarrow$  2,1-C<sub>10</sub>H<sub>7</sub>(NH<sub>2</sub>)N(O)NAr (VI). VI with O  $\rightarrow$  II or with the loss of H<sub>2</sub>O  $\rightarrow$  naphthotriazole C<sub>10</sub>H<sub>7</sub>:N<sub>2</sub>Ar (VII). But VII is also obtained by direct oxidation from I. Once formed VI remains unchanged

in part, reacts to give VII in part and the remainder is transformed according to Wallach into *o*-aminohydroxyazo derivs. (VIII) and this in turn is oxidized, giving 2, *N*-*p*-hydroxyphenyl  $\alpha$ ,  $\beta$ -naphthotriazole from which C. and C. conclude that VIII is 1,2,4- $C_{12}H_7(N-NPh)(NH_2)OH$ . A certain amt. of 2-nitro-1-naphthol, m. 128°, which is formed by diazotisation of the azo group with  $H_2O_2$  (C. A. 9, 1316) and oxidation of the  $NH_2$  to  $NO_2$  (Bamberger, Tschirner, *Ber.* 32, 1675 (1899); C. A. 19, 2192) is always formed. A good part of the VII formed undergoes further oxidation, forming 2, *N*-aryltriazolyl phenyl- $O_2$ -dicarboxylic acids (IX) and if  $H_2O_2$  is allowed to act for a week this reaction is complete. If much excess  $H_2O_2$  is used, besides much II a dark red product, m. above 360°, that is probably a trisazo deriv., is obtained. II are quite similar to the corresponding benzo derivs. in most of their reactions; they are easily reduced with HI and Zn dust + AcOH to the corresponding naphthotriazoles; they are oxidized to IX with alk.  $KMnO_4$  but are resistant to  $H_2O_2$  + AcOH which act easily upon VII. 100 g. 1,2- $C_{12}H_7(N-NPh)NH_2$  (X) was dissolved in 1700 cc. glacial AcOH, treated with 300 cc. perhydrol (Merck) and warmed on the  $H_2O$  bath at 60-70° for 3 hrs, until gas ceased to be evolved and then 3 hrs. at 100° until gas evolution ceased. The cold soln. was poured into  $H_2O$ . The spongy viscous ppt. was washed well with  $H_2O$  and when dry extd. with  $Et_2O$ . The  $Et_2O$  soln. was agitated with 20% NaOH. The  $Et_2O$  was then called portion A, the red-brown NaOH soln. portion B and the residue fusol. in  $Et_2O$  portion C. The  $H_2O$ -AcOH soln. gave a thick sirup on evapn. This sirup in EtOH treated with NaOH sepd. the mono-Na salt of the 2, *N*-Ph deriv. of VII, m. 242°. Portion A after concn. was allowed to stand some days and sepd. 2, *N*-phenyl- $\alpha$ ,  $\beta$ -naphthotriazole oxide (XI), m. 146°, previously described. The mother liquors from XI evapd. and taken up in EtOH sep. 2, *N*-phenyl- $\alpha$ ,  $\beta$ -naphthotriazole, m. 107°. These EtOH mother liquors on further treatment yield an isomer of XI, colorless, m. 196.5°, differs from XI by being sol. in alk. solns. and being reprecipitated unchanged, does not give the reaction of XI with  $H_2SO_4$  (s. e., a yellow color in cold and a red to brown color in hot  $H_2SO_4$ ), and is thought to be 1,2,4- $C_{12}H_7(N-NPh)(NH_2)OH$ , arising by a Wallach transposition. Portion B was acidified with HCl, the brown resin was dried in the air and extd. with  $Et_2O$ . From this ext. the above Na salt of a VII, m. 242°, was sepd. The mother liquors were evapd. and when distd. in steam gave 1,2- $HOC_6H_4N_2O_2$ , m. 128°. Portion C was a yellow powder sol. in EtOH and on evapn. sepd. an azoxyamino deriv., m. 206°, which is 2,1- $C_{12}H_7(NH_2)N(O).NPh$  or 2,1- $C_{12}H_7(NH_2)N(N(O)Ph)$  or both and is to be studied further. Details of 2 oxidations of X under other conditions referred to above, are given; qual., the results are the same. 1-*o*-Tolylazo-2-aminonaphthalene treated as with X gave by the same methods of sepn. 2, *N*-*o*-tolyl-1,2-naphthotriazole oxide (XII), m. 166.5°, and 2, *N*-*o*-tolyl-1,2-naphthotriazole, m. 96° (also obtained from XII with Zn + AcOH). 1-*p*-Tolyl-2-aminonaphthalene gave 2, *N*-*p*-tolyl-1,2-naphthotriazole oxide, m. 117°; 2, *N*-*p*-tolyl-1,2-naphthotriazole, m. 148-9°; one or two 1-*p*-tolylazoxy-2-aminonaphthalene (analogous to that obtained with X), m. 206°; 2, *N*-*p*-tolyltriazolylphenyl- $O_2$ -dicarboxylic acid, m. 233°; and probably 2, *N*-*p*-tolyl-1,2-naphthotriazole-4-hydroxylate,  $HOC_6H_4.N_2C_6H_4Me$ , m. 274°. 1-*p*-Bromophenylazo-2-aminonaphthalene gave 2, *N*-*p*-bromophenyl-1,2-naphthotriazole oxide, m. 205°; 2, *N*-*p*-bromophenyl-1,2-naphthotriazole, m. 200°; 2, *N*-*p*-bromophenyltriazolylphenyl- $O_2$ -dicarboxylic acid, m. 270°; 4-hydroxy-2, *N*-*p*-bromophenyl-1,2-naphthotriazole, m. 245°. 1-*p*-Chlorophenylazo-2-aminonaphthalene gave 2, *N*-*p*-chlorophenyl- $\alpha$ ,  $\beta$ -naphthotriazole oxide, m. 200°; 2, *N*-*p*-chlorophenyl- $\alpha$ ,  $\beta$ -naphthotriazole, m. 186°; and 2, *N*-*p*-chlorophenyltriazolylphenyl- $O_2$ -dicarboxylic acid, m. 264-5°. Details of the oxidation of XI with alk.  $KMnO_4$  to what is probably 2, *N*-phenyloxytriazolylphenyl- $O_2$ -dicarboxylic acid,  $HOCC_6H_4.C_6H_4O(Ph)CO_2H$ , m. 243°, are given. 2, *N*-Phenyl- $\alpha$ ,  $\beta$ -naphthotriazole treated with AcOH +  $H_2O_2$  gave not a trace of II, but considerable 2, *N*-phenyltriazolylphenyl- $O_2$ -dicarboxylic acid, m. 242°.

E. J. WITTEMAN

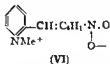
Pyridone methide. OTTO MUMM, K. BEHRENS, A. v. FISCHER-TREUENFELD, G. HINGST, W. LUND, O. MROZEK, J. SÖNKESEN AND O. TONN. *Ann.* 443, 272-309 (1925).—The term pyridone methide has been applied to a group of compds. contg. a  $CH_2$  side chain, which may also be termed methylenedihydropyridines or methylenepyridans. They result by the action of NaOH upon the methineide or methosulfate, through the quaternary  $NH_4$  base and the pseudo-base. The same is specially employed for 1,6-dimethyl-3,5-dicarbethoxy-2-pyridone methide, which has a H in the  $\gamma$ -position; compds. with substituents in the  $\gamma$ -position are called  $\gamma$ -ethylpyridone methide, etc. The following methosulfates were prepd.: *di-Et parrolinedicarboxylate*, m. 130.5°; *di-Et isobutylindinedicarboxylate*, sinters 103°; m. 115°; 4-furyl deriv., m. 152-3°; 4-Ph deriv., m. 150-2°. The ice-cold concd. soln. of the methosulfate with somewhat more than the calcd. amt. of KCN gives the pseudocyanide: 1,5-dimethyl-3,5-dicarbethoxy-2-pyridone.

m. 131°,  $\gamma$ -Et deriv., m. 92°,  $\gamma$ -isobutyl deriv., m. 67°;  $\gamma$ -*p*-methoxyphenyl deriv., m. 117-8°,  $\gamma$ -*m*-nitrophenyl deriv., m. 151.5°. NaOH and the methosulfates, under slightly varying conditions, give 80-90% of the pyridone methides: 1,6-dimethyl-3,5-dicarboxy, isolated as the perchlorate, m. 110°. 4-Et deriv., light yellow, m. 78° (perchlorate, m. 115°); 4-*iso*-Bu deriv., yellow, m. 47° (perchlorate, m. 140-1°; picrate, yellow, m. 117-8°); 4-furyl deriv., reddish brown, m. 81° (perchlorate, m. 156-7°; picrate, yellow, m. 119-20°); 4-Ph deriv., red, m. 110-1° (decompn.) (perchlorate, m. 191-2°); 4-*p*-methoxyphenyl deriv., yellow-red, m. 94-5°; 4-*m*-nitrophenyl deriv., dark red, m. 76-8° (perchlorate, m. 158-9°). The 4-furyl deriv. in EtOH adds 2 atoms I; in  $C_6H_6$ , shaking with O adds 2 atoms O, giving a peroxide,  $C_{10}H_{10}O_2N$ , dark brown, strongly hygroscopic powder. Shaken with 2 N NaOH pyridone methide gives 1,6-dimethyl-3-acetyl-5-carboxy- $\alpha$ -pyridone (I), m. 131° (phenylhydrazone, m. 194°); 4-Me deriv. phenylhydrazone (II), m. 191-2°; 4-isobutyl deriv., m. 87°; 4-furyl deriv., m. 137° (phenylhydrazone (III), m. 204-5°); 4-Ph deriv., m. 141-2°; 4-*p*-methoxyphenyl deriv., yellowish white, m. 126-7° (phenylhydrazone, m. 231-2°); 4-*m*-nitrophenyl deriv., m. 137-8° (phenylhydrazone, m. 188-9°). Heating I with 2 N NaOH (or by boiling pyridone methide with NaOH) gives 1,6-dimethyl-3-acetyl-5-carboxy- $\alpha$ -pyridone, m. 255°; 4-Et deriv., by heating the pseudocyanide with NaOH, m. 201°; 4-*iso*-Bu deriv., m. 209-10°; furyl deriv., m. 220-2° (decompn.), 4-*p*-methoxyphenyl deriv., m. 237°. I, slowly heated with an equal wt. of concd.  $H_2SO_4$  to 180-200°, gives 1,6-dimethyl- $\alpha$ -pyridone, m. 352°. 4-Furyl deriv., m. 153.5°.  $\gamma$ -Methylpyridone methide and  $PbNH_2$  give II; the  $\gamma$ -furyl deriv. gives III. Reduction of  $\gamma$ -ethylpyridone methide in hexane with Pt and H gives a small amt. of the sym. di-Et N-methyldihydropyridine dicarboxylate, m. 89°, insol. in dil. HCl, but principally the unsym. dihydro deriv., light yellow, m. 52°. The corresponding unsym.  $\gamma$ -*iso*-Bu deriv. is an oil, b.p. 140°; the  $\gamma$ -furyl deriv., yellow, m. 98°; the  $\gamma$ -Ph deriv., yellow, m. 127-8°;  $\gamma$ -*p*-methoxyphenyl deriv. (IV), yellow, m. 106-7°;  $\gamma$ -*m*-nitrophenyl deriv., yellow, m. 112-3°. Reduction of the  $\gamma$ -furyl methosulfate with Na-Hg in  $H_2O$  gives the sym.  $\gamma$ -furyl deriv., m. 96°. Further reduction of IV in AcOH by Pt and H gives the tetrahydro deriv., yellow oil, b.p. 200-1°.  $\gamma$ -Phenylpyridone methide and excess MeI give di-Et 6-methyl-2-ethyl-4-phenylpyridinedicarboxylate methiodide, yellow, m. 167° (decompn.). [Di-Et phenylpyridinedicarboxylate methiodide, yellow, m. 173-4° (decompn.)].  $Me_2SO_4$  behaves similarly, giving the methosulfate, m. 160-1°, which, with 10 N NaOH, yields the compd.  $C_{14}H_{12}O_4N$ , m. 108-10° (decompn.) (perchlorate, m. 173°), which may be 1,6-dimethyl-4-phenyl-3,5-dicarboxypyridone ethide or the isomeric 1-methyl-6-ethylmethide. This adds 1 mol.  $Me_2SO_4$ ; the methosulfate, m. 160-1° and yields with NaOH a pyridone methide,  $C_{14}H_{12}O_4N$ , m. 107-8° (perchlorate, m. 167-8°). Pyridone methides add  $CS_2$  with the loss of EtOH, giving good yields.  $\gamma$ -Ethylpyridone methide  $CS_2$  product,  $C_{10}H_{10}O_4NS$ , red, m. 181° (HCl salt, light yellow; perchlorate, light yellow).  $\gamma$ -*iso*-Bu deriv., red-violet, m. 198-200° (the yellow HCl salt is stable only in concd. HCl);  $\gamma$ -*p*-methoxyphenyl deriv., violet, m. 229-30°. They also react with PhNCS, with the loss of EtOH; pyridone methide PhNCS compd.,  $C_{11}H_{10}O_4NS$ , dark red, m. 261°; the Me deriv., carmine-red, m. 264-5°; Et deriv., red, m. 239° (decompn.). (di-HCl salt, yellow needles which lose 1 HCl over soda lime after 10 days; perchlorate, yellow); *iso*-Bu deriv., red, m. 221° (HCl salt, light yellow, very unstable in moist air; both mols. HCl are lost in vacuum at 100°); furyl deriv., dark red, m. 233-5°; *p*-methoxyphenyl deriv., dark red, m. 273° (decompn.); *m*-nitrophenyl deriv., dark red, m. 247° (decompn.). PhCNO in EtO first forms an addn. compd. which, boiled a short time with EtOH, loses 1 mol. EtOH, giving the cyclic compd. Pyridone methide gives a cyclic compd.,  $C_{11}H_{10}O_4N$ , m. 251°;  $\gamma$ -Me deriv., addn. compd. with 1 PhCNO, m. 137-9° (decompn.) with loss of EtOH, giving the cyclic compd., m. 212-3° (HCl salt of addn. compd., m. 182°); addn. compd. with 2 PhCNO, red, sinters 122°, m. 135°; this gives 2 cyclic compds., yellow, m. 228-9°, and brownish red, sinters 145°, m. 158-60°.  $\gamma$ -Et deriv., addn. compd., reddish yellow, m. 131°; cyclic compd., yellow, m. 217° (HCl salt, yellow needles);  $\gamma$ -*iso*-Bu deriv., addn. compd., brown, m. 117-9°; cyclic compd., yellow, m. 227-8° (HCl salt); if the reaction is carried out in EtO, there results an isomeric cyclic compd., yellow, m. 161°;  $\gamma$ -furyl deriv., addn. compd., red-brown or yellow, m. 157-8°; cyclic compd., brick-red, m. 257-8°;  $\gamma$ -methoxyphenyl deriv., addn. compd., m. 169°; cyclic compd., brick-red, m. 295-300°;  $\gamma$ -*m*-nitrophenyl deriv., addn. compd., yellow, m. 151-2°; cyclic compd., eosin-red, m. 283°.

C. J. WEST

Pyridone methides. ERNST KOENIGS, KURT KÖHLER and KURT BLINDOW. *Ber.* 58B, 933-40(1925).—When N, $\alpha$ - or N, $\beta$ -dialkylpyridinium salts are treated with alkalis the quaternary hydroxides first formed change into the deeply colored, very reactive alkylene-N-alkyldihydropyridines for which Mumm and Hingst have sug-

gested the name pyridone methides (C A 18, 1127). K, K, and B. have found that when the mixt. of  $\alpha$ - and  $\gamma$ -benzylpyridines (I and II) obtained by the Chichibabin and Riumshin synthesis is nitrated and the derivs. of the resulting  $\alpha$ - and  $\gamma$ -*p*-nitrobenzylpyridines (III and IV) are treated with alkyl halides there is observed a very characteristic color which was ascribed to the formation of pyridone methides. Thus, the methiodides treated with just enough alkali to neutralize the HI at once give dark blue ppts having the compn. of nitrobenzylidene-*N*-methylpyridans (V). They can be recrystd. from alc. and neither their smooth quant. formation without an excess of alkali nor their stability agrees with the properties hitherto observed of the pyridone methides. The methiodides of the I and II themselves begin to change into the methides at a much lower concn. of alkali than observed by Decker (Ber. 38, 2493(1905)); even before the amt. of KOH necessary to combine with the III has been added the  $C_6H_5$  layer assumes a faint yellow color on shaking; as also observed by D., the yellow  $C_6H_5$  soln. of the methide is decolorized by shaking with much  $H_2O$ . Comparison of the properties of these compds. with those obtained from III and IV does not establish with certainty the constitution of the latter; possibly the lability of the H atoms of the  $CH_2$  group is considerably increased by the introduction of a  $NO_2$  group and the tendency to methide formation is thereby increased. In favor of structure V against that (VI) of a betaine-like deriv. of a nitronic acid is the soly. of the deeply colored anhydro base in  $Et_2O$  and  $C_6H_6$ ; against it, the fact that III forms with alc. NaOH a deep cherry-red soln. which probably contains the Na salt of the oxi-form. Preference is given to the methide structure (V). To obtain light on the mechanism of the methide formation, the reaction was applied to the benzylidene- $\alpha$ - and  $\gamma$ -benzylpyridines (VII and VIII),  $C_6H_5NC(:CHPh)Ph$ , in which the side-chain C atom involved in the methide formation carries no H atom. The methiodides of these compds. behave with alkali in the same way as those of I-IV, although with somewhat greater difficulty.  $BzH$  is smoothly split off and benzylidene-*N*-methylpyridans (IX), identified as their  $PhNCS$  addn. products, are formed. Stilbazole behaves in the same way. III, m.  $76^\circ$ , will be described in detail elsewhere; methiodide, m.  $248^\circ$ , can be obtained from the brown product of the reaction between III and MeI at  $100^\circ$  by extg. with hot  $H_2O$ , but as it is thereby partially decompd. it was not isolated but converted with hot dil. HCl into the methochloride, yellowish, m.  $240^\circ$ , which with dil. NaOH gives  $\alpha$ -V, dark blue flocks, m.  $160^\circ$ .  $\gamma$ -V, pptd. from dil. HCl by NaOH as a dark blue powder, decomp.,  $50^\circ$ . II, MeI, from the mixt. of I and II with MeI at  $0^\circ$ , m.  $121-2^\circ$ , quite sensitive to light and moisture; the mother liquors yield a mixt. of II, MeI and I, MeI. To obtain the latter pure  $\alpha$ - $p$ - $H_2NC_6H_4C_6H_5N$  is diazotized, cautiously poured into an excess of cold NaOH, carefully treated with alk.  $SnCl_2$ , distd. with steam and the resulting I treated with MeI at room temp.; the I, MeI m.  $116-7^\circ$ . The 2 methiodides cannot be recovered from their aq. solns. and boiling alc. also decomp. them.  $PhNCS$  compd.,  $MeNC_6H_4C(CSNHPh)Ph$ , of  $\gamma$ -IX, yellow, blackens about  $145^\circ$ , m.  $162^\circ$ ; of  $\alpha$ -IX, reddish, m.  $147-8^\circ$ . VII, oil; HCl salt, m.  $196-7^\circ$ ; picrate, yellow, m.  $165-6^\circ$ , easily sol. in alc.; methiodide, light yellow, m.  $173-3^\circ$ . VIII, m.  $86^\circ$ ; HCl salt, m.  $216-7^\circ$ ; picrate, m.  $189-9^\circ$ , less sol. in alc. than the  $\alpha$ -isomer; methiodide, m.  $212-3^\circ$ . Stilbazole-MeI, m.  $215-6^\circ$ .



C. A. R.

Optical properties of coniline hydrochloride. GEO. L. KEENAN AND R. M. HANN. *J. Am. Chem. Soc.* 47, 2063-4(1925).—Attention is called to the value of optical properties for the identification of cryst. compds. Coniline-HCl has  $\alpha$  1.535,  $\gamma$  1.540; the extinction is parallel, the sign of elongation negative; in convergent polarized light biaxial interference figures are common and the optic axial angle is  $30-5^\circ$ . Dispersion is very marked, red being greater than violet. In parallel polarized light many of the fragments show yellow interference colors (1st order), but some show peculiar and characteristic blues or purples (anomalous interference colors).

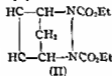
C. J. WEST

Quinoline and the centroid formula. R. C. FUSON. *J. Am. Chem. Soc.* 47, 2018-21(1925); cf. C. A. 19, 495.—Attention is called to the existence of a quinoline compd. which contains a *peri*-bridge, viz., the lactam of 5-aminocinchoninic acid (Koenigs and Lossow, Ber. 32, 717(1899)). The orientation assigned to this compd. is shown to be correct. 8-Hydroxycinchoninic acid was prepd. by the method of Weidel and Cobenzl (Monatsh. 1, 814(1880)) and its orientation verified; the pure acid, m.  $258-9^\circ$ ; attempts

to dehydrate this acid, thus causing it to form a 4,8-bridge, have failed. From these data it is concluded that  $C_8H_7N$  cannot have the centroid structure proposed by Huggins. From this it is inferred that the centroid structure is untenable for  $C_8H_7$  and aromatic nuclei in general.

C. J. WEST

The endo-methylenepiperidazine resulting from cyclopentadiene and azo ester and its transformation into 1,3-diaminocyclopentane. OTTO DIELS, J. H. BLOM AND WERNER KOLL. *Ann.* 443, 242-62 (1925).— $EtO_2CN: NCO_2Et$  (I) and dimethylisoprene give *N,N'*-dicarbethoxy-3-dimethyl-5-methyltetrahydropyridazine,  $b_p$ , 136°; Br adds readily but the bromide easily splits off  $HBr$ , giving resinous products. I and cyclopentadiene give 90-5% of *N,N'*-dicarbethoxy-endo-methylenetetrahydropyridazine (II),  $b_p$ , 121°,  $b_s$ , 125°,  $b_l$ , 132°,  $b_{12}$ , 133°, solns in acids are pptd unchanged by alkali. Dibromo deriv., m. 67°. Reduction of II with Pd and H in EtOH gives *N,N'*-dicarbethoxy-endo-methylenepiperidazine (III),  $b_p$ , 120°,  $b_s$ , 123°,  $b_l$ , 127°,  $b_{12}$ , 131°, m. 42°; it does not react with Br and is fairly stable towards  $KMnO_4$ . Conc'd HCl at 100° for 1.5-2 hrs gives with 10 g. III 4.8 g. *N,N'*-dicarbethoxy-3-methyl-5-chloropiperidazine,  $b_p$ , 155°, m. 90°. III and 25% MeOH-KOH on the  $H_2O$  bath give 82% of Me endo-methylenepiperidazine-*N* carboxylate,  $b_p$ , 133°, very hygroscopic. Picrate, yellow, m. 176-7°. Further heating with 25% MeOH-KOH for 1-1.5 hrs gives 70% of endo-methylenepiperidazine (IV),  $b_p$ , 65-8°,  $b_{12}$ , 162°, it is strongly auto-oxidizable, it colors moist litmus paper blue and forms very sol salts with mineral acids. Aq IV with



$CuCl$  at first decolorizes the Cu salt, the soln then becomes wine-red and after long standing there ppts. the dark earmine or red cuprochloride,  $C_8H_7N_2 \cdot CuCl \cdot 0.5H_2O$ , of endo-methylenedehydropiperidazine (V), m. 99-99.5°, obtained from the  $CuCl$  salt by excess conc'd NaOH. V also gives a red cuprobromide. Methiodide, Au-yellow. Reduction of V with  $SnCl_2$  in 20% HCl gives IV, isolated as the chlorostannate, m. 224-9°. The above  $CuCl$  deriv., reduced with Sn and conc'd HCl, gives *cis*-cyclopentylene-1,3-diamine-HCl (VI), isolated as the  $SnCl_4$  salt, crystg with 1  $H_2O$ , m. 172°. Decompd. with conc'd NaOH and evapd with HCl, there results *cis*-cyclopentylene-1,3-bis-carbamide (VII), m. 230-3° (217-21° on slow heating) (decompn) *cis*- $C_4H_8(CO_2Me)_2$ ,  $b_p$ , 124-5°, with  $N_2H_4 \cdot H_2O$  gives *cis*-cyclopentane-1,3-dicarboxylic dihydrazide, m. 205-6°;  $NaNO_2$  and dil HCl give the diazide, which gives with EtOH the diurethan, this was not purified, but transformed into VI and this in turn into VII. The compd. of cyclopentadiene and quinone absorbs 2 atoms H, giving the compd  $C_8H_7O_2$ , sinters 185-8°, m. 190-1°. Dicyclopentadiene quinone absorbs 4 atoms H, giving the compd.  $C_{10}H_{10}O_2$ , sinters 220-30°, m. 239-43° (decompn).

C. J. WEST

Cuprous halide molecular compounds of azo compounds. OTTO DIELS AND WERNER KOLL. *Ann.* 443, 262-72 (1925); cf preceding abstr.—Because of the  $CuCl$  salt described above, it became important to prep similar compds. of simple azo compds.  $(MeNH)_2 \cdot 2HCl$  in an excess of 2  $N$  AcONa, treated with  $CuCl$  soln until the soln contains an excess as shown by its dirty olive green color, gives the brick-red azomethane cuprochloride,  $C_4H_9N_2 \cdot CuCl$ , decomp. into its components upon heating. Azoisopropane cuprochloride,  $C_6H_{11}N_2 \cdot CuCl$ , red, with 2  $H_2O$ . It is decompd. by washing with  $Et_2O$  and then has the approx compn.  $C_6H_{11}N_2 \cdot 2CuCl$ . 3,5,5-Trimethyldehydropyrazolidine also gives an orange ppt. with  $CuCl$ , which was not further investigated.

C. J. WEST

Octahydrophenazine. MARCEL GONCHOR. *Compt. rend.* 180, 444-6 (1925).—From 28 g. of  $\alpha$ -chlorocyclohexanone (I) in abs. alc., 8 g. of octahydrophenazine (II) is obtained by the action of dry  $NH_3$  at room temp., followed by evapn, extrn. with HCl, and pptn of II with dil KOH. The  $NH_3$  reacts to form the  $\alpha$ - $NH_2$  deriv., which condenses to the decahydro compd, the latter giving II by spontaneous oxidation. II, yellowish, m. 107-8°, its solns. having a blue fluorescence; the di-Br deriv., formed in  $CCl_4$ , m. approx. 70° (decompn), the picrate, m. 167-8°, the HCl salt, m. 116-7°; heated with MeI in MeOH at 100° for 6 hrs. II forms a violet-green methiodide, m. approx. 150° (decompn). Attempts to prep homologs of II from Me derivs. of I gave products that could not be sepd, being apparently highly condensed compds.

WM. B. PLUMMER

Synthesis of apomorphine. J. GADAMER, M. OBERLIN AND A. SCHOETTER. *Arch. Pharm.* 263, 81-90 (1925).—The ultimate purpose of this investigation was not alone a

During the AcOH treatment, the II is converted to III, which is then rearranged to abietic acid. III has 2 double bonds, one of which can be easily reduced. When reduced with Pt black and  $H_2$ , II and III both give a dihydro compd., which has a sharp m p (182–3°) and does not undergo change on treatment with hot AcOH, or HCl (unlike the reduced product of abietic acid). III has a retene group  $C_{15}H_{14}$  and is likely an isomer of abietic acid. S. T.

Disaccharins. H. J. CROUPOER. *Proc. Acad. Sci. Amsterdam* 28, 119–26 (1925).—See C. A. 19, 2195. H. G.

The halogenated proteins. IV. Bromofibrin. A. J. J. VANDEVELDE. *Rec. trav. chim.* 44, 224–8 (1925), cf. C. A. 19, 818.—Fifteen g. of dry fibrin (13.1% N) was placed in 100 cc.  $CCl_4$ , contg. 3 cc. dry  $Br_2$ . The wt. of the fibrin increased gradually to 25.5 g. in 270 days. The bromofibrin obtained contained 41.1% Br and 8.06% N; after heating the dry compd. at 100° it contained 35.4% Br and 11.0% N. Treatment with  $H_2O$  or NaOH gave products less rich in Br but of variable compn. Like the 3 bromoproteins previously studied (C. A. 18, 2134, 2501; 19, 818), the soln. of bromofibrin contains HBr, but a certain variable amt. of Br remains organically combined. It is curious that bromofibrin heated forms products insol. in  $H_2O$  that are richer in Br. E. J. WITZEMANN

BOURGEOIS, L. Recherches sur les bromures d'ammoniums quaternaires dérivés de la benzhydrylamine. Paris: Les Presses Univ. de France, 68 pp.

X ray diffraction effects from solid fatty acids (WYCKOFF, *et al.*) 2. Asymmetric cleavage of polypeptides by enzymes (ABDERHALDEN, SINGER) (ABDERHALDEN) 11A. Presence of a S compound in some grades of commercial benzene which contain no thiophene (PARISI) 21.

## 11—BIOLOGICAL CHEMISTRY

PAUL E. HOWE

A—GENERAL

FRANK P. UNDERHILL

Diastase. W. SYNIEWSKI. *Bull. Internat. Acad. Pol. Sci. Lettres* 1924, 131–43.—It has been shown previously that the diastase present in barley ext. hydrolyzes only the  $\alpha$ -carbonyl linkings of the starch mol. and is hence an  $\alpha$  diastase, setting free all the maltose residues from the starch and leaving only the non-reducing "limit dextrin I," which with I gives a blue coloration equal in intensity to that given by starch.  $\alpha$ -Diastase is destroyed by heating the ext. at 60° for 20 mins. The  $\beta$  diastase of malt arises only during malting, and is not completely destroyed until a temp. of 80° is reached. That this  $\beta$ -diastase is a natural enzyme and not an artificial product is shown by the fact that the action on starch of a mixt. of barley ext. with malt ext. previously heated at 78° corresponds exactly with that of non-denatured malt ext. B. C. A.

Action of  $\alpha$ -diastase on the so-called amylopectin. W. SYNIEWSKI. *Bull. Internat. Acad. Pol. Sci. Lettres* 1924, 145–8.—The existence of the author's non-reducing "limit dextrin I," which is the source of the dextrins formed when starch is hydrolyzed with diastase (C. A. 19, 1250), might be regarded as a proof of Maquenne's amylose amylopectin theory of the constitution of starch granules. The author finds, however, that Gatin-Gruzewski's amylopectin is hydrolyzed by the  $\alpha$ -diastase of barley ext. in exactly the same way as Maquenne's amylose (the author's amylopectin, identical with sol. starch), the products consisting of maltose and the author's non-reducing limit dextrin I, identity between the latter and amylopectin is, therefore, impossible. B. C. A.

Source of error in the use of Lintner's starch solution for determining diastatic power. W. SYNIEWSKI. *Bull. Internat. Acad. Pol. Sci. Lettres* 1924, 149–51.—When Lintner's starch is used for the detn. of diastatic activity, low values for the latter are obtained, as an appreciable quantity of diastase may be present without hydrolysis occurring. The error introduced in this way increases with the age of the starch soln., and appears to depend on adsorption of diastase by suspended colloidal particles of reversion products of the starch. B. C. A.

Deamination of aspartic acid by hydrolysis. G. ARLGREN. *Compt. rend. soc. biol.* 90, 1187–90 (1921).—Contrary to the general opinion that the deamination of amino

acids in the organism takes place by way of an oxidative process, A. holds that aspartic acid can undergo deamination through a hydrolytic process. This view is based on its reaction with methylene-blue in frog muscle. If the muscle is washed, aspartic acid is without action. Otherwise reduction takes place, but only to an equal condition, as with fumaric and malic acids. Complete reduction takes place with oxalacetic acid and with alanine. It is supposed that aspartic acid is changed into malic acid by a deaminase present in muscle which is readily removed by washing. B. C. A.

**Kinetics of hemoglobin. III. Velocity with which oxygen combines with reduced hemoglobin.** H. HARTTRIDGE AND F. J. W. ROUGHTON. *Proc. Roy. Soc. (London)* 107A, 654-83 (1925); cf. C. A. 18, 87.—The following methods were employed to prep. large quantities of reduced hemoglobin soln. (1) one l. of sheep's blood was agitated in a 20 l. evacuated bottle at 40° several times, the gas phase being removed each time; (2) blood was freed from O by spraying into an evacuated glass container at 50°; (3) in the alk. range ( $p_H = 10$ ) the addn. of 1%  $(NH_4)_2S$  soln. caused complete reduction of oxyhemoglobin. Identical results were obtained with reduced hemoglobin by each of the above methods. Water contg. dissolved O and the reduced hemoglobin soln. were mixed by the methods previously described and the course of the reaction was followed spectroscopically at different places on a tube through which the mixt. was flowing at a known rate. The reaction is very rapid, the time for half completion being 0.01 to 0.001 second. The velocity const. with different mixts., both where  $p_H = 7$  and  $p_H = 10$  or 11, showed that the reaction is bimol. Neither change of salt concn., H-ion concn. nor temp. caused any marked effect on the velocity const. The suggestion that the reaction might be photochem. was, however, found to be erroneous. The possibility of the existence of aggregates in soln. was examd. and the conclusion reached that the presence of such aggregates will not affect the velocity of O uptake so long as the part of the hemoglobin with which the O combines is sharply localized and far removed from the part of the grouping which forms aggregates. If in addn. it is assumed that every collision of O with this localized portion results in combination an explanation is offered for the low temp. coeff. JAMES M. BELL

**The influence of purification of enzymes on their sensitivity toward irradiation.** LUDWIG PINCUSSEN. *Fermentforschung* 8, 181-6 (1925).—Pancreatic diastase was purified by successive treatments of the crude glycerol ext. of the gland with  $H_2O$ ,  $AcOH$  and  $Al(OH)_3$ , kaolin,  $EtOH$  and dialysis, and at each step in the purification the diastatic activity was detd. before and after exposure to the rays from a quartz Hg lamp. With progressive purification there was also a progressive increase in the destructive action of the violet rays. The diastatic activity of the crude ext. was only slightly diminished by 15 min. irradiation, whereas after the 7th stage of purification 30 min. irradiation destroyed 85% of the enzyme present. A. W. DOX

**Asymmetric cleavage of polypeptides by means of enzymes.** EMIL ABDERHALDEN AND WALTER SINGER. *Fermentforschung* 8, 187-93 (1925).—Only those polypeptides which are comprised wholly of naturally occurring amino acids are hydrolyzed by enzymes. With racemic mixts. the isomer which contains 1 or more amino acids of opposite rotation to that of the natural form remains intact. Four racemic tripeptides were thus sepd. into one of the isomers, and a mixt. of amino acids resulting from cleavage of the other isomer, by means of yeast inactivation. *dl*-Alanylglycylglycine gave *d*-alanine, glycine and *l*-alanylglycylglycine,  $m$  220°,  $[\alpha]_D^{20} -32.5^\circ$ . *dl*-Leucylglycylglycine gave *l*-leucine, glycine and impure *d*-leucylglycylglycine,  $m$  225°,  $[\alpha]_D^{20} -5^\circ$ . Glycyl-*dl*-leucylglycine gave *l*-leucine, glycine and impure glycyl-*d*-leucylglycine showing a slight *l* rotation, but the cleavage was far from complete. The tripeptide, *dl*-leucylglycyl-*dl*-alanine, consists of 2 racemic mixts. which were sepd. from each other by their different soly. in dil.  $EtOH$ . The 1st, which contains *l*-leucylglycyl-*d*-alanine and *d*-leucylglycyl-*l*-alanine (I), was hydrolyzed into *l*-leucine, glycine, *d*-alanine and I,  $m$  250°,  $[\alpha]_D^{20} -17.2^\circ$ . The 2nd mixt., consisting of *d*-leucylglycyl-*d*-alanine and *l*-leucylglycyl-*l*-alanine, was not attacked, since only traces of free amino acids could be detected. In the 4 instances where hydrolysis occurred the products were sepd. by pptg. the unaltered isomeric tripeptide with phosphotungstic acid, and the free amino acids remaining in the filtrate were identified by the prepn. of characteristic derivs. A. W. DOX

**Asymmetric cleavage of racemic polypeptides by enzymes.** EMIL ABDERHALDEN. *Fermentforschung* 8, 240-4 (1925).—Racemic tetra- and pentapeptides undergo asymmetric cleavage through the action of yeast infusion in the same manner as do the simpler di- and tripeptides. *dl*-Alanyldiglycylglycine gave *d*-alanine, glycine and 75% of *l*-alanyldiglycylglycine (I), decmps. 250°,  $[\alpha] -28.5^\circ$ . *dl*-Leucyltriglycyl-

glycine gave l-leucine, glycine and 68% of *d*-leucyltriglycylglycine (II),  $[\alpha] -27^\circ$ . No intermediate polypeptides could be demonstrated among the products of hydrolysis. The sp. rotations of I and II were in close agreement with those of the previously described isomers, but of opposite sign.

A. W. DOX

Observations on the enzyme content of the liver of normally nourished and of fattened geese, EMIL ARDERHALDEN. *Fermentforschung* 8, 194-6(1925).—The fattened livers contained more lipase, less glycogenase and maltase and less protease (silk peptone and *dl*-leucylglycine) per g. of material than did the normal livers. No especial significance is attached to these observations since the basis of comparison is not satisfactory. The results would not be strictly comparable unless made on the basis of equal nos. of cells. Detns. of total N and ash were considered as a possible measure of the relative no. of cells, but were found to be unreliable.

A. W. DOX

The influence of insulin on the fermenting power of yeast cells. EMIL ARDERHALDEN. *Fermentforschung* 8, 227-31(1925).—Alc. fermentation of glucose, fructose, galactose, sucrose and maltose is accelerated by insulin, but to a smaller extent than by products obtained from yeast, such as yeast autolysate or substances isolated therefrom.

A. W. DOX

The distribution of linamarase, LEOPOLD ROSENTHALER. *Fermentforschung* 8, 279-81(1925).—Linamarase, an enzyme which hydrolyzes linamarin into glucose, HCN and MeAc, was found in 47 of the 50 fruits and seeds examd., none of which contained the glucoside. The enzyme is not identical with emulsin, sucrase, maltase or diastase.

A. W. DOX

Enzymes of the lima bean, LEOPOLD ROSENTHALER. *Fermentforschung* 8, 282-3(1925).—An enzyme prepn. from *Phaseolus lunatus* hydrolyzed starch, maltose,  $\alpha$ -methylglucoside, amygdalin and sucrose.

A. W. DOX

The nature of the substances which give rise to the formation of protective enzymes in the organism. G. FRANZEN. *Fermentforschung* 8, 303-25(1925).—Expts. with rabbits showed that injection of protein preps. from testes and ovaries result in the formation of protective enzymes, though not invariably. Less conclusive results were obtained with thymus, thyroid, hypophysis and suprarenal glands. Possibly hormones as well as proteins are responsible for the formation of protective enzymes. It is not improbable also that the sp. proteins of the glands contain unknown amino acids or simple complexes of non protein character which play the role of hormone precursors.

A. W. DOX

Pancreatic enzymes. XIII. The  $p_H$  optimum of the gastric lipase of various animals. FELIX HAUKOWITZ AND WILHELM PETROV. *Z. physiol. Chem.* 144, 68-75(1925); cf. C. A. 19, 1873.—After purification human gastric lipase resembles that of the dog and is more active in alk. than in acid medium. The  $p_H$  optimum shows remarkable constancy for each species of animal examd. For carnivorous animals, also for hares and rabbits, it lies between 5.5 and 6.3; for rodents and for the mole, horse and hog, between 7 and 8; for birds and fishes, between 7.9 and 8.6. The lipase content varies widely, being greatest in carnivora and rodents and less in birds and fishes. In ruminants and pigeons it is apparently absent.

A. W. DOX

Enzymic degradation and synthesis of carbohydrates. II. HANS V. EULER, KARL MYRHÄCK AND RAGNAR NILSSON. *Z. physiol. Chem.* 144, 137-46(1925); cf. C. A. 19, 1716, 2071.—Alc. fermentation ( $p_H$  8) of glucose occurs with all the fresh yeasts examd., both top and bottom. With dried yeasts an essential difference was noted; top yeasts gave a strong fermentation at  $p_H$  8, while bottom yeast H was entirely inactive. Addn. of phosphate had no appreciable effect either in neutral or alk. medium. The fermentation of pyruvic acid by bottom yeast H is strongly inhibited at  $p_H$  8.5, while sugar fermentation still proceeds with great velocity. At  $p_H$  8.5 autolysis does not occur. Top yeast R is more active toward pyruvic acid under the same conditions.

A. W. DOX

Brominated keratin and oxykeratin. II. ZDANKO STARY. *Z. physiol. Chem.* 144, 147-77(1925); cf. C. A. 18, 2719.—Human hair, which is one of the most resistant keratin substances, was subjected to the prolonged action of Br in AcOH, on the one hand, and of  $H_2O_2$  in 4 N  $H_2SO_4$  on the other hand, at room temp. The main products were high-molecular, protein-like substances, easily sol. in alkali and precipitable by acids, quite const. in compn. and easily hydrolyzed by trypsin. While keratoses, prepd. by the action of alkali or acid, give a strong carbonyl reaction with both picric acid and  $CaH_2(NO_3)_2$ , the above products give no such reaction. Compared with the original substances the reaction products contain more  $NH_2$ - and humin-N, though not to the extent of the usual oxidation products of proteins. The monoamino acids are essentially intact, probably because of the milder oxidizing agents employed. Since

polypeptide chains are hydrolyzable by trypsin, it is assumed that these result from the opening up of ring systems. They are of high mol. wt. as shown by pptn reactions and low  $\text{NH}_2$  index, and more complex than keratin peptones, which are not appreciably hydrolyzed by trypsin. The increased O content of the reaction products suggests the cleavage, under oxidation, of partially reduced ring systems which are characterized by the CO reaction and resistance to proteolytic enzymes. A. W. DOX

Study of the Amhard phenomenon (fixation of amylase by starch). F. CHODAT AND M. PHILIA. *Compt. rend. séances soc. phys. hist. nat. de Genève* 41, 118-22(1924); *Physiol. Abstracts* 9, 557.—The statement of Amhard, that starch grains will completely "fix" the amylase from a solution, is inaccurate. A variable, but appreciable quantity of the enzyme remains in soln. H. G.

A widely distributed substance (plasmal, plasmalogen), its histological demonstration and its relation to the odor of cooked meat. R. FEULGEN AND K. VORT. *Klin. Wochschr.* 4, 1330(1925).—Plasmalogen is a lipid, contained in the protoplasm of animals, that is oxidized to an aldehyde (plasmal) by  $\text{HgCl}_2$  or by air in the presence of acids or when heated. Plasmal immediately restores the color of decolorized fuchsin. It m.  $20^\circ$ , gives a cryst. semicarbazone and has a characteristic odor. M. H.

Enzyme action. XXIV. The oxidase effect and the phenomena of oxidation in general: carbonic oxide, H. E. ARMSTRONG. *Proc. Roy. Soc. (London)* 98B, 202-6 (1925).—The oxidases are catalysts, but not true enzymes since their action usually is not strictly selective. Adrenaline has a selective action on sympathetic centers and, like an enzyme, controls oxidation at these centers. JOSEPH S. HEPBURN

Photochemical reaction of urine. A. VON SOÖS. *Z. klin. Med.* 98, 347-52(1924); *J. Chem. Soc.* 126, 1, 1373.—Certain substances are present in dark urines, and apparently function as protective colloids, inhibiting the action of photographic developers on AgCl which has previously been exposed to light. JOSEPH S. HEPBURN

How salt preserves. GEO. E. ROCKWELL AND E. G. EBERS. *J. Infectious Diseases* 35, 573-5(1924).—The preserving of proteins with salt involves more than its dehydration effect, there being at least 4 factors, namely, dehydration, direct effect of Cl ion, removal of O, sensitization against  $\text{CO}_2$  and interference with rapid action of proteolytic enzymes. JULIAN H. LEWIS

Insulin. H. B. LEWIS. *Ann. Clin. Med.* 3, 623-33(1925).—General discussion of the ductless glands and of the developments which led to the discovery of insulin. JOHN T. MYERS

Factors affecting transmission and recovery in the passive iron nerve model. R. S. LILLIE. *J. Gen. Physiol.* 7, 473-507(1925).—The speed of transmission of the activation wave along passive Fe wires (C. A. 14, 73, 3682) enclosed in glass tubes contg. 70%  $\text{HNO}_3$  soln. increases with the cond. (sectional area) of the electrolyte. The speed is nearly proportional to the sq. root of the cond., i. e., the rate of transmission increases more slowly than the cond. The divergence between speed and cond. is due to the tendency of the electrode area on the passive side of the passive-active boundary to become proportionally smaller as the intensity of the local current increases. "After an interval of partial or decremental transmission (having high temp. coeff. and lasting several min. at  $20^\circ$ ), the wire recovers its power of transmitting an activation wave for an indefinite distance. In such a recovered wire, the speed of transmission is at first slow and increases by degrees up to a max., the increase following a curve apparently of the type  $v_t = v_0(1 - e^{-kt})$ . The approx. time required to attain this max. (corresponding to complete recovery) at the different temps. is 15 to 20 min. at  $20^\circ$ , 30 to 45 min. at  $15^\circ$ , about 60 min. at  $10^\circ$ , and 90 min. or more at  $5^\circ$ ." The increase in speed probably depends on a progressive chem. change in the mols. of the passivating film. This change involves the transformation of relatively non-reactive into reactive mols., the change following the course of a monomol. reaction. The temp. coeff. of the speed of transmission between  $5^\circ$  and  $10^\circ$  is low ( $Q_{10} = 1.3-1.6$ ), but for the rate of recovery, it is high (about 3). Analogous conditions in nerve and other transmitting protoplasm are discussed. "Passive wires inclosed in acid-contg. continuous and interrupted glass tubes immersed in a large vol. of acid exhibit characteristic phenomena of distant action; under appropriate conditions the velocity of transmission of the activating influence between different areas may thus be greatly increased. Characteristic instances are cited and some possible physiol. parallels are pointed out." CHAS. H. RICHARDSON

The mechanism of change in resistance of erythrocytes to hypotonic salt solutions. S. C. BROOKS. *J. Gen. Physiol.* 7, 587-98(1925).—KCl causes a greater loss in resistance to hypotonic hemolysis than NaCl regardless of the species from which the cells are taken. KCl and NaCl do not have opposite effects on the red blood cells, depending

on whether the cells are K-rich or K-poor, as Ashby (*C. A.* 18, 2904, 2005) has maintained  
CHAS. H. RICHARDSON

A test for diffusible ions. II. The ionic nature of pepsin. J. H. NORTHROP. *J. Gen. Physiol.* 7, 603-14 (1925), cf. *C. A.* 18, 844—Procedure: For the pepsin soln., 10 g. Park Davis  $1/10,000$  pepsin are placed in 100 cc.  $H_2O$ , titrated to  $pH$  2 with  $HNO_3$  soln. and dialyzed against 0.01  $N$   $HNO_3$  soln. for 3 days after which the soln. is brought to  $pH$  3.0. *Detn. of pepsin*:—The relative quantity of pepsin was detd. according to Northrop and Hussey (*C. A.* 17, 1260), except that 0.2 cc. samples were used to 10 cc. gelatin and also a 2 cc. viscometer. The standard gelatin soln. contained 1.3% gelatin and 0.066  $M$   $H_3PO_4$ . The unit of pepsin is that quantity which causes a 10% decrease in 10 cc. of the standard gelatin soln. in 1 hr. at  $34^\circ$ . "The distribution of pepsin between particles of gelatin or coagulated egg albumin and the outside soln. has been found to be equal to the distribution of Cl or Br ion under the same conditions. This is the case from  $pH$  1 to 7, and in the presence of a variety of salts. Pepsin is therefore probably a univalent anion. Under certain conditions the enzyme may be absorbed on the surface of the protein particles. This reaction is irreversible and is markedly influenced by the presence of low concns. of electrolytes." CHAS. H. RICHARDSON

Iodine in sea air. A. LOIR AND H. LEGANGNEUX. *Bull. acad. med.* 93, 343 (1925); *J. Am. Med. Assoc.* 84, 1531—I in the sea air is stated to be in the org. form. At a certain depth in sea water I is in inorg. combination, but at the surface the combination is org. The sea air, due to the fact that the sea weeds, etc., yield I to the air by their spores and debris, contains 13 times as much I as the air of Paris. The tonic action of the sea air is attributed in part to the org. I which is assumed to be easily assimilated.  
L. W. RIGGS

Disequilibria of concentration caused by diffusion. E. DEMOUSSY. *Compt. rend.* 180, 1359-61 (1925), cf. *C. A.* 18, 1076—Solns. of 0.2, and 0.1  $N$   $HCl$  were stratified on solns. of 0.2, 0.5 and 1.0  $N$   $Ca(AcO)_2$  and the compns. of the top and bottom layers were detd. after 10 to 12 days. A soln. mixt. of  $HCl$  and  $Ca(AcO)_2$  was placed in parchment sacks, the latter were placed in  $HCl$  of the same concn. as that in the mixt. and the compn. of the liquid on each side of the parchment was detd. after various periods of time. An attempt was made to harmonize the changes in compn. of the liquids used in these expts. and the relations of the compn. of cell sap to that of its exterior medium.  
L. W. RIGGS

Presence of nickel and of cobalt in animal tissues. GABRIEL BERYRAND AND M. MACHREBOEUR. *Compt. rend.* 180, 1380-3 (1925).—Ni was detd. in combination with dimethylglyoxime in comparison with known amts. of Ni. This method was sensitive to  $1/100$  mg. of Ni. In certain human tissues Ni ranged from 0.09 mg. in the liver to 0.022 in the brain per kg. of fresh tissue. In muscle, fat, stomach and uterus its presence was uncertain. Ni was found in the tissues of the bull, fowls, fish, lobster, mollusks and tunicates, being most abundant in the mussel (0.455 mg. per kg.). Co was often present but its quantity was not detd.  
L. W. RIGGS

Coagulation of casein in the presence of calcium salts in acid solution. L. LEXLEY. *Compt. rend.* 180, 1462-3 (1925)—It appears that milk which is faintly acid (less than 2 g. lactic acid per l.) is on the verge of coagulation, but this acidity has not dissolved enough of the Ca compds. to establish coagulation. An increase of acidity either naturally or artificially allows the Ca caseino-phosphate in the presence of acid to coagulate the casein but the acid alone does not bring this about since it dissolves the curd. This soly. cannot be measured as a colloidal soln. is formed. Various complexes of calcium caseinate-calcium phosphate and their modes of action toward rennet. CH. PORCHER. *Ibid.* 1534-6—To obtain coagulation of Ca caseinate by rennet it is necessary to add an insol. salt capable of passing into the colloidal condition and of forming with the caseinate a stable combination. The rapidity and completeness of casein coagulation are closely dependent upon the quantity of Ca phosphate in the complex.  
L. W. RIGGS

Contributions of pure science to professional medicine. WM. J. MAYO. *J. Am. Med. Assoc.* 84, 1465-9 (1925)—Presidential address. The contributions of pure science to medicine, in the great majority of cases, have been made by chemists. L. W. R.

The intensity sensation of sound according to the ionic theory of excitation. P. LAZAREV. *Compt. rend.* 180, 1526-7 (1925)—It appears necessary to admit the existence of substances in the cells around the fibers of Corti, which react under the influence of vibrations of those fibers, and which produce during this reaction the ionic excretors of the auditory nerves.  
L. W. RIGGS

Iron, the oxygen-carrier of respiration enzyme. OTTO WARBURG. *Science* 61, 575-82 (1925); cf. *C. A.* 19, 1711.—It is maintained that in respiring cells there is a cycle

in the form of Fe(bivalent) mol. O Fe (of higher valence) org. substance Fe (bivalent).  
 —————→ L. W. RIGGS

Proteins as electrolytes. L. HALLION. *J. pharm. chim.* [8] 1, 339-49, 355-91 (1925).—A résumé based on Loeb's *Proteins* (C A 16, 3098) of the chem. and phys. properties of protein as an amphoteric electrolyte. S. WALDBOTT

Relations of the physical properties of proteins with their functioning as electrolytes. L. HALLION. *J. pharm. chim.* [8] 1, 480-91 (1925).—The phys. properties considered, on the basis of Loeb's treatise (cf. preceding abstr.) are soly., osmotic pressure, swelling and viscosity. S. WALDBOTT

The basis for the physiological activity of certain onium compounds (BENCOWITZ, RENSIAW) 2. Halogenated proteins (IV) bromofibrin (VANDEVELDE) 10.

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## B—METHODS AND APPARATUS

STANLEY K. BENEDICT

Colorimetric determination of acetone in urine. M. H. P. SITSEN. *Pharm. Weekblad* 62, 622-3 (1925).—To 50 cc. of urine add 10 cc. basic Pb acetate soln. Add 10 cc. of 10%  $\text{Na}_2\text{HPO}_4$  to 30 cc. of the filtrate, dil. to 50 cc. and filter through a triple filter. The filtrate is colorless and corresponds to  $\frac{1}{2}$  the vol. of urine. To 5 cc. of this decolorized urine add 2 cc. of 5% Na nitroprusside soln. and 5 cc. 4 N NaOH and mix, then add 10 cc. 30% AcOH and dil. to 50 cc. By means of a colorimeter compare the red color with that of 0.0005% MeAc soln. treated simultaneously in the same manner. The method is not applicable to urines contg. phenolphthalein or istizin (synthetic purgatives). A. W. DOX

Detection of adrenaline in urine. LABAY AND FAVREAU. *Bull. soc. pharm. Bordeaux* 63, 102-7 (1925).—The following methods for the detection of adrenaline were tested: Iodic acid method of Frankel and Allers; method of d'Abelous, Soulié and Toujan; of Zanfognini; of Pancrazio, of Denigès. The last method carried out as follows was found to be the most satisfactory. Add 5 cc. of a satd. aq. soln. of  $(\text{AcO})_2$  and 1.0 g. of  $\text{AcONa}$  to 10 cc. of urine, shake vigorously during 1 min. and place in a boiling water bath for 10 to 15 seconds. Shake and cool by plunging the tube in cold water. Filter. The fugitive rose color of the filtrate, if adrenaline is present, will endure sufficiently long for a good observation. This method is sensitive to 0.005 mg. of adrenaline per l. From the examn. of a large number of urines, it is concluded that, if adrenaline is a normal constituent, it is present in quantities too small to be detected by the methods devised up to the present time. A. G. DUMÉZ

Photographing microscopic changes in pressure and volume. K. MORI. *Acta Schol. Med. Univ. Imp. Kioto* [III] 6, 327-31 (1924).—An app. with which microscopic manometric changes in cerebrospinal fluid or volumetric change in the uterus, bladder, heart, or stomach of frogs and dogs can be accurately measured. W. F. GOEBEL

New methods of demonstrating changes in the tone of the arterioles. R. J. S. M'DOWALL AND B. L. WORSNOP. *Quart. J. Exptl. Physiol.* 15, 181-6 (1925).—The use of acetylcholine is suggested because it gives indication of changes in arterial pressure. There is an increased reaction to acetylcholine when the capillaries are dilated by histamine. FRANCES KRASNOW

Effect of sodium carbonate concentration in the Benedict sugar method. A. J. QUICK. *Ind. Eng. Chem.* 17, 729-30 (1925).—In Benedict's volumetric method for the detn. of sugar in urine, for any concn. of  $\text{Na}_2\text{CO}_3$  greater than 25 g. per 100 cc. of the final soln., the reagent has a const. minimal oxidizing value, but for lower concn. the value increases with the decrease in concn. of the  $\text{Na}_2\text{CO}_3$ . The action of  $\text{Na}_2\text{CO}_3$  is not sp. but is due to its OH-ion concn., since the same effect may be brought about by adding  $\text{Na}_3\text{PO}_4$  to increase alkali. The minimal oxidizing value was found to be somewhat lower than that reported by Benedict, 1 cc. of the reagent being equiv. to 1.88-

190 mg. glucose instead of 20 mg. The application of these findings to the analysis of dil. sugar solns. is pointed out. H. B. LEWIS

**Cholesterol content of bile in health and disease.** I. Methods for collection and estimation in the duodenal contents of man. C. W. McCLEURE. *Bost. Med. Surg. J.* 188, 633-5(1923).—This is a preliminary paper in which the technic of obtaining bile and estg. the cholesterol are described. JULIAN H. LEWIS

**Effect of alkaloids and salts upon vital staining.** I. Living tissues. A. BORNSTEIN AND ELISABETH RÜTER. *Arch. ges. Physiol.* (Pflüger's) 207, 596-613(1925).—Alkaloids and  $\text{NH}_4\text{Cl}$  are very effective, neutral salts and  $\text{HCl}$  are less active (or inactive) in decolorizing parameria, leucocytes and erythrocytes. Some alkaloids, and neutral salts and  $\text{HCl}$  modify the staining of muscle cells and of plant tissues. Unquestionably the permeability of the cell for the poisonous substance plays a role in the elective action of the substances in decolorization. II. ELISABETH RÜTER AND A. BORNSTEIN. *Ibid.* 614-23.—The basic dyestuffs (neutral red, methylene blue, Nile blue) can be removed from cellular protoplasm by alkaloids, the decolorization in a way indicates microscopically the penetration of alkaloids into animal and plant cells. Neutral salts exert a similar effect. Usually they are less active than the alkaloids, but occasionally their activity is very strong. Of the nonelectrolytes studied sucrose is least active. Of the animal tissues, erythrocytes and white blood cells, amebae, and parameria form a single group as regards the ability of alkaloids to effect decolorization, muscle cells and plant cells form a second group. Dyestuffs which have combined with dead org. and inorg. adsorbents can be decolorized in a similar way, a differential action being manifest in that certain adsorbents behave as do the blood cells, others reacting like muscle cells. Here also, just as with living cells, nonelectrolytes are less effective than electrolytes. G. H. S.

**Application of electrical conductivity to quantitative biochemical analysis (DEM'YANOVSKI) 7.**

KOLMER, JOHN A. and BOERNER, FRED: *Laboratory Diagnostic Methods, Pathological, Bacteriological, Serological, Chemical*. London: Appleton & Co. 362 pp. 10s 6d

## C—BACTERIOLOGY

A. E. BALLS

**Nitrification in acid solutions.** T. GAARDER AND O. HAGEM. *Bergens Museums Aarbok* 1922-1923; *Naturvidensk. række* No. 1, 26 pp.; cf. *C. A.* 17, 2027.—By selective culture, strains of bacteria have been obtained which can produce nitrites from  $(\text{NH}_4)_2\text{SO}_4$  at various H-ion concns. The following bacteria have been distinguished: *Bact.*  $\alpha$ , optimum pH 7.7-7.9, min. pH 7.0-7.1; *Bact.*  $\beta$ , optimum pH 6.8-7.0, min. pH 6.6; *Bact.*  $\gamma$ , optimum pH 6.5-6.6, min. pH 6.0-6.1; probably also a bacterium with optimum pH 7.0-7.2. It is not certain if the nitrification in acid solns. is the work of 1 or of 2 bacteria. B. C. A.

**Radiometric investigation of the germicidal action of ultra-violet radiation.** W. W. COBLENTZ AND H. R. FULTON. U. S. Bur. Standards, *Sci. Paper* 19, No. 495, 641-80(1924). E. J. C.

**Experiments on the conversion of cellulose, lignin and wood into humins by fungi.** C. WEINER. *Brennstoff-Chem.* 6, 101-6(1925).—Pure lignin (with and without added sugar or malt ext.) was allowed to remain in contact with the fungi (*Coniophora cerebella*, *Polyporus caporarius*) in K phosphate and  $\text{MgSO}_4$  soln. for a year.  $\text{NH}_4\text{NO}_3$  was also added as a N source. Pure lignin did not support development of the fungus; this developed when malt or sugar had been added, but any lignin also present remained unchanged. With the fungus *Merulius lacrymans* and pure cellulose (filter paper) humification did not take place; the soln. did not change blue litmus nor was there brown coloration with alkali. With newspaper pulp (contg. both cellulose and lignin), however, there was extensive humification and the cellulose content sank from 50 to 12.5%. W. thinks the presence of certain enzymes is required for humification, which are present in wood fiber but not in pure lignin or cellulose. Photomicrographs are given which show shrinkage of cell walls of wood which has been exposed to the fungus. The experiments do not prove conclusively that lignin is the parent substance of humins and hence also of coal, but W. thinks the evidence points in this direction. J. D. DAVIS

**Fermentation with partially poisoned yeast.** HANS VON EULER AND VERA SANDBERG. *Fermentforschung* 8, 232-9(1925).—The fermentation velocity is diminished 50% by the presence of 0.03-0.05 N  $\text{PhOH}$  in 2 cc. of glucose soln. contg. 0.1 g. fresh yeast. The cell proliferation is diminished 10% by 0.015 N and completely inhibited

by 0.017 *N* PhOH. There is therefore a considerable toxicity range between inhibition of growth and inhibition of fermentation. Normally, glucose and maltose are fermented under the same conditions at the same rate, but in the presence of 0.04 *N* PhOH the maltose fermentation is completely suppressed while the glucose fermentation is diminished by half. This difference is explained on the assumption that an active maltase is necessary for the cleavage of maltose before a synthesis of zymophosphate can occur. The evidence contradicts Willstätter's hypothesis that maltose undergoes a direct fermentation.

A. W. DOX

**Coproporphyrin synthesis by yeast and factors which influence it.** II. Analysis of crystallized coproporphyrin copper from fresh yeast and the increase of porphyrin by additions. HANS FISCHER AND HERMANN FINK. *Z. physiol. Chem.* 144, 101-22 (1925); cf. *C. A.* 19, 310.—Both zymocasein and cerevisin prepd. from autolyzed yeast were found to contain coproporphyrin as the Cu salt. The total yield was 21 mg. from 50 kg. of fresh press yeast, and a microanalysis of the cryst. prepn. showed the formula  $C_{44}H_{34}O_8N_4Cu$ . The presence of Cu is attributed to the use of brass vessels in the brewery. The remarkable affinity of coproporphyrin for heavy metals, especially Cu, suggested a study of the effect of heavy metals on the synthesis of this porphyrin by yeast. The fact that brewer's yeast, although grown on wort contg. Cu from contact with Cu vessels, never contains porphyrin as the Cu salt leads to the inference that the porphyrin is a constituent of the cell and not a secretion or an excretion. Addns. of small quantities of Cu, Fe, Pb, As and V salts to the culture medium lead to an increase in the quantity of porphyrin synthesized by the yeast. Concns. of Cu up to 1:100,000 do not retard growth, and in this respect yeast is less sensitive than other microorganisms. Where coproporphyrin was obtained as the Cu salt it is believed that the Cu complex was formed during the process of isolation. The occurrence of Kämmerer's porphyrin in summer yeast cannot be attributed to the presence of insects, since a sep. examn. of flies after autolysis, putrefaction and acid hydrolysis gave no evidence of this porphyrin, although coproporphyrin was easily detected.

A. W. DOX

**Hydrogen-ion concentration and peptones used in bacteriology.** E. M. CHAMOR AND F. R. GEOROLA. *J. Am. Water Works Assoc.* 13, 661-74 (1925).—Difficulties were experienced in obtaining satisfactory and concordant results in media prepd. from various brands of peptones. After considerable exptl. work, 3 brands are recommended for indole production. These are Armour's, "Witte," and "Proteose" in the order named. Much other data are recorded, including the  $pH$  of different peptone solns. with the addn. of alkali or acid.

D. K. FRENCH

**The synthetic ability of pathogenic bacteria and their biological reactions under simple nutritive conditions.** III. The significance of metabolism in the dispensability or indispensability of oxygen. H. BRAUN AND C. E. CAPEN-BRONNER. *Centr. Bakt. Parasitenk., I Abt. Orig.* 86, 380-92 (1921); *Abstracts Bact.* 7, 153; cf. *C. A.* 17, 2722.—Previous expts. of the authors have shown that a medium of 0.5% NaCl, 0.2%  $K_2HPO_4$ , 0.6%  $NH_4$  lactate, neutralized with  $NaHCO_3$  to litmus and 0.7% *N* soda soln. added, supports the growth of aerobes, but not anaerobes. To det. what amendment was necessary to support anaerobic growth, organic N compds. and higher C compds. were added. With *B. paratyphosus* B and *B. paratyphosus* A under anaerobic conditions, both groups of bacteria are quite similar, requiring an amino acid and a carbohydrate in order to live without O. The authors discuss the relation of true anaerobic growth as shown by *B. paratyphosus* A and B with pseudo-anaerobiosis as manifested by *B. pyocyaneus* which under anaerobic conditions reduces the nitrates for its O supply.

H. G.

**Energy requirements for nitrogen fixation by nodule bacteria in comparison to other nitrogen fixation possibilities and initial studies of the subject.** P. CHRISTIANSEN-WENIGER. *Centr. Bakt. Parasitenk., II Abt.* 53, 41-66 (1923); *Expt. Sta. Record* 49, 812-3.—A review is given of the results of work of others, and studies are reported to det. the energy requirements of nodule bacteria during the process of the fixation of air N. The energy requirements of nodule bacteria were not met by the increased assimilating powers of treated legumes. It was not possible to exclude the factor of growth acceleration in plants treated with N. The upper limits for the energy requirements of nodule bacteria in N fixation were established by this means, however. The results are taken to indicate that the eventual energy requirement of nodule bacteria is so small as to be unimportant. This is considered to be of special significance in connection with recent attempts to adapt nodule bacteria to crops other than legumes, and to indicate that their energy requirements will not react injuriously to such plants to any noteworthy extent. Conclusion: The process of N fixation by nodule bacteria is exothermic. In this connection an est. of the energy requirements indicated that they

were hardly sufficient to support the life activities of the bacteria, and that the requirements of nonsymbiotic bacteria were 5 times as great. It is considered probable, therefore, that nodule organisms are so constituted as to be able to transform some of the energy incident to an exothermic N fixing process into life energy. H. G.

The utilizable metabolism of acid-fast bacteria. III. The food requirements of avian-tubercle bacillus: its growth by synthesis from simple chemical compounds. S. KONDO. *Biochem. Z.* 153, 302-12(1924).—Avian-tubercle bacillus did not utilize  $\text{HCO}_2\text{H}$ ,  $\text{AcOH}$ , lactic or butyric acids when used as their Na salts or free lactic, succinic, malic, tartaric and citric acids, but did utilize free  $\text{AcOH}$  as a source of C.  $\text{MeOH}$ ,  $\text{EtOH}$ ,  $\text{AmOH}$  and mannite were not utilized. Glycerol did sustain life, although not growth. With glucose, levulose, or arabinose alone, no passage was obtained. As a source of N, both  $\text{NH}_3$  and  $\text{NaNO}_3$  served. As a single source of C and N, the following amino acids were tried: glycocoll,  $\beta$ -alanine, aspartic acid, asparagine, L-leucine and L-tyrosine. In no case was passage obtained. Neither urea nor uric acid was utilized for growth. Avian-tubercle bacillus, therefore, has a smaller no. of utilizable foodstuffs than saprophytes and cold blooded tubercle bacillus. W. D. LANGLEY

Oxygen indicators in bacteriology. E. RUST KADTSCH. *Centr. Bakt. Parasitenk., I Abt.* 90, 462-8(1923).—Methyl-*p*-aminophenol, 1,2,4-diaminophenol, *p*-aminophenol, and *p*-hydroxyphenylglycine act as indicators of O when added to agar media. Increase in indicator properties runs parallel with the substitution no. of amino groups and with the increase of the no. of the latter. All suitable indicators bear the substitution in the *p*-position. The groups of the nucleus are of more importance than the substitutions in the side-chains. The substances mentioned above are superior to methylene blue as O indicators because they are indicators themselves and require no manipulation after being added to agar, and their relative O-binding properties are greater. They prevent the entrance of O into the media and eventually bind that already present, and a part of them shows no disturbing color changes. J. H. L.

In vitro studies on the bactericidal action of hexal and neohepal. J. BRINKMANN. *Centr. Bakt. Parasitenk., I Abt.* 91, 420-44(1924).—The bactericidal action of hexal and neohepal, sulfosalicylic acid derivs. of urotropine, was shown to be only moderate when tested on coli, *B. typhosus*, Shiga-Kruse dysentery bacillus, *Staphylococcus aureus*, *Streptococcus hemolyticus*, pneumococcus, diphtheria bacilli and the diplococcus of Wiener. The action is weakened by physiol. salt soln. and still further diminished by proteins. This diminution rests on the chem. binding of the active components, formaldehyde and sulfosalicylic acid, particularly by the proteins. No selective action for any particular organism was observed. The bactericidal action is due to the formaldehyde resulting from the hexamethylenetetramine under the influence of the sulfosalicylic acid. This is in common with other urotropine derivs. J. H. L.

Etiology of over-oxidation. ALEXANDER JANKE. *Centr. Bakt. Parasitenk., II Abt.* 59, 305-10(1923).—Over oxidation is the transformation of alc. into  $\text{AcOH}$  and then  $\text{CO}_2$  and is accomplished by so-called  $\text{AcOH}$  bacteria and contaminating organisms. Besides the organisms that are known to be able to accomplish this an alga and an achlorotic *Chlorophyceae* (*Prototheca* species) are also capable. An acid-forming *Mycoderma* species was found, and although it was not highly resistant to the acid formed it could exist in the casks where over-oxidation occurs because of the formation of dry esters, or because of unequal mixing of the mash. It may also grow in symbiosis with mucus bacteria. JULIAN H. LEWIS

Propionic acid fermentation in Emmenthal cheese of Russian manufacture. A. WOJTKIEWICZ. *Centr. Bakt. Parasitenk., II Abt.* 59, 333-6(1923).—The propionic acid bacteria isolated from Russian Emmenthal cheese were compared with those from Switzerland. They were similar in all respects except in the fermentation of lactose which proceeded more energetically in the former. More acetic than propionic acid was produced in Russian cheese. It is impossible to say if these differences were responsible for the inferior quality of Russian cheese. JULIAN H. LEWIS

Is the ability to utilize citrate readily acquired or lost by the colon-aerogenes groups? S. A. KOSER. *J. Infectious Diseases* 35, 315-22(1925).—*B. coli* isolated from soil is able to grow in a citrate medium (C. A. 18, 1512) while that isolated from feces is not. The ability to utilize citrate is apparently a fairly stable character, and evidently is not readily acquired or lost. The citrate differentiation, to sep. the intestinal *B. coli* from other members of the colon group, appears to be quite const. and reliable. J. H. L.

Toxico-immunologic and serologic relationship of *B. botulinus*, type C, and *B. paratyphosus*, "Seddon." XXII. W. FENNINGER. *J. Infectious Diseases* 35, 347-60(1924).—The inability of type C and "para" strains to grow on anaerobic blood plates renders the estn. of the growth rate a difficult and complicated procedure. In liquid

media the development is frequently spasmodic and thus far uncontrollable. The changes in amino acid,  $\text{NH}_3$  and non-protein N of C and *parabotulinus* strains are slight. The ability of the organisms to autolyze has been demonstrated by microscopic and biochem tests. Exo-enzymes of the same character as those found in types A and B are not demonstrable in the type C cultures. The weak proteolytic activities are due to autolytic enzymes activated by the constituents of the medium. The comparatively slight utilization of sugar is evidence of the low metabolism of types C and *parabotulinus*. The toxin production of a pathogenic sporulating anaerobe is not necessarily associated with bacterial proteolysis.

JULIAN H. LEWIS

"Hormone" media. Simple method of preparation and value of hormone blood agar for preserving pneumococci and streptococci. SARIE F. BILLY. *J. Infectious Diseases* 36, 340-2(1925).—The method of making "hormone" medium which is described produces a medium which is rich in growth producing factors because the agar has already been melted and cooled when brought into contact with the raw uncoagulated-meat particles, the growth factors are retained because they are not removed by the manner of filtration or by overheating, it is economical because the meat is removed by filtration so that the relatively large amt of medium usually cut off and thrown away is saved, and is clear and free from discoloration because the reaction is not adjusted until after the meat has been removed. Sixty-two cultures of pneumococcus and 32 cultures of streptococcus were kept alive for 12 months without transplantation, on modified hormone blood agar slants in tubes sealed with paraffin kept in the light at room temp.

JULIAN H. LEWIS

Growth of *B. botulinus* in 30% peptone. XXVII. With notes on Van Slyke's amino nitrogen method for study of bacterial metabolism. PEARL BRISTOL. *J. Infectious Diseases* 36, 457-71(1925).—Concd media are superior to dil. ones for quant. studies of bacterial metabolism because they permit greater chem. activity of the bacteria and the high N content is conducive to greater accuracy in analysis. Concs. of peptone above 30% are inhibitive to *B. botulinus*, but in 25% peptone approx 4 times as many bacteria are produced as in 2% peptone. The toxin production in 25% peptone and 2% peptone is equal provided both cultures are incubated the same length of time after visible growth appears. Centrifugalization is preferable to filtration for the removal of bacteria from cultures to be analyzed.  $\text{NH}_3$  and amino acid N methods were investigated experimentally, and Van Slyke's amino N method was found valuable for the detn. in culture media. In the detn. of  $\text{NH}_3$ , 1% NaOH was found to be the best concn. of alkali for liberating  $\text{NH}_3$  without hydrolysis. The most evident changes occurring in the growth of *B. botulinus* in a 25% Difco peptone and 0.5% NaCl soln. are the following: A decided decrease in the protein and peptide N fractions and a tremendous increase in  $\text{NH}_3$  N. The  $\text{NH}_3$  production is practically equiv. to the protein and peptide disintegration which indicates that deamination of the amino acids is responsible for most of the  $\text{NH}_3$  formed. The decrease in the protein and peptide N is a measure of the proteolytic and peptolytic activity of *B. botulinus*. J. H. L.

The causes for variation in  $p_{\text{H}}$  in cultures of *B. diphtheria*. G. ABY AND G. LOISEAU. *Ann. inst. Pasteur* 39, 114-43(1925).—The diphtheria bacillus cultivated in Martin's bouillon produces much  $\text{CO}_2$ . More than half is liberated from the medium during growth. The remainder is about equally divided in the medium as dissolved  $\text{CO}_2$  and as bicarbonate. The dissolved  $\text{CO}_2$  is partly ionized, and increases the acidity of the medium by more than  $p_{\text{H}}$  1.0. However, no const. relation exists between the  $p_{\text{H}}$  and the amt. of dissolved  $\text{CO}_2$ . The bicarbonates exert only a feeble direct influence on the reaction of the medium, but have an important buffering effect. The diphtheria bacillus destroys AcOH preferably, and BnOH and lactic acid less readily. Formic acid is the most resistant to its action. In the course of growth simultaneous production and destruction of acids occur, the former predominating during the first 2 days, the two being equal the next 2 days, and destruction being more active thereafter. The high initial production of acid and the simultaneous accumulation of  $\text{CO}_2$  are responsible for the early acidification of alk media. Progressively increasing alk. is the result of 3 factors, production of  $\text{NH}_3$ , conversion of org. acid salts into bicarbonates, and the transformation of primary into secondary phosphates. In media originally acid the phase of acidification is suppressed by the rapid destruction of org. acids, and the effect of the  $\text{NaHCO}_3$  formed. The zone  $p_{\text{H}}$  7.0-7.4 is a critical one, that being the region where satn. of the phosphates requires the most alkali.

E. R. LONG

Effect of radium in vitro on *Treponema duttoni*. R. BRUYNOGUE AND A. DUBOIS. *Compt. rend. soc. biol.* 92, 466(1925).—The  $\beta$ - and  $\gamma$ -radiations have a feeble effect; Ra emanation (5 millicuries) makes the treponemas innocuous after an exposure of 5-23 hrs.

S. MORCULIS

The origin of  $\beta$ -hydroxybutyric acid obtained by bacterial process. LEMOIGNE *Compt rend* 180, 1539-41 (1925); cf. *C. A.* 19, 2221.—Certain bacteria, on autolyzing, give rise to  $\beta$ -hydroxybutyric acid from an intracellular substance which is only slightly diffusible. An organism designated as "Bacillus M" was shown to contain, in the unautolyzed form, an amorphous substance which may be isolated with chloroform and which, upon saponification, will yield  $\alpha$ -crotonic acid. This product is the mother substance from which  $\beta$  hydroxybutyric acid is formed during the process of autolysis due to diastatic hydrolysis. G. F. REEDISH

The stimulating action of certain organic compounds on cellulose decomposition by means of a new aerobic microorganism that attacks both cellulose and agar. P. H. H. GRAY AND C. H. CHAMBERS. *Annals Appl. Biol.* 11, 324-38 (1924).—A new microorganism, *Microspira agar-liquefaciens*, has been found which decomposes cellulose (filter paper) and agar-agar with great rapidity. It is able to utilize these substances as the sole source of energy for growth and retains its power to decompose them for at least 9 months in the lab. The presence of small quantities of certain other carbohydrates increases the decompn. of filter paper. The stimulating effect of xylose and lignin is of interest in view of their presence with cellulose in straw. C. H. R.

"Fruitiness" in whey. I. Bacterial studies. II. Chemical studies. E. R. HISEOX AND K. LOMAX. *Annals Appl. Biol.* 11, 503-13 (1924).—This is a description of a case of "fruitiness" due to the interaction of a bacillus and a yeast. During fermentation, the bacillus hydrolyzed the lactose with the production of glucose and galactose, while the yeast was without action on lactose but caused alc. fermentation of the products of bacterial hydrolysis. The fruity odor was caused by a mixt. of  $\text{CH}_3\text{CHO}$ , alc. and  $\text{AcOH}$ . The  $\text{CH}_3\text{CHO}$  is formed by oxidation of the  $\text{EtOH}$  by the yeast. Fruitiness was reproduced in cheese contg. *B. bulgaricus* and the yeast. CHAS. H. RICHARDSON

Symbiosis between *Chlorella* sp. and *Azotobacter chroococcum* and nitrogen fixation. C. B. LIPMAN AND L. J. H. TEAKLE. *J. Gen. Physiol.* 7, 509-11 (1925).—Mixed cultures of these organisms showed a high efficiency in the fixation of N. C. H. R.

The acid agglutination of mixtures of oppositely charged bacterial cells. L. T. WEASTEA. *J. Gen. Physiol.* 7, 513-5 (1925).—Two suspensions of *Bacterium leptosepticum*, one of which was stable and possessed a high negative charge, the other, less stable and possessing a very low negative charge, were combined in various proportions and buffered with Na lactate soln. at  $\text{pH}$  2.4-4.7. Agglutination of the mixed suspensions took place in the intermediate  $\text{pH}$  zone,  $\text{pH}$  3.8-4.1. The H-ion concn., at which 1 suspension is negatively and the other positively charged, furnishes the proper conditions for the optimum flocculation of the mixt. The results of this study support the theory that bacteria with like charges are repelled. CHAS. H. RICHARDSON

The culture of *Aspergillus niger* with special reference to the buffer effects of the medium. T. SAKAMURA. *J. Coll. Agr. Hokkaido Univ. Tokyo* 14, Pt. 2, 65-128 (1924).—S. has shown how changes in  $\text{pH}$  of the medium affect the shape of the mold. A  $\text{pH}$  of about 2 was best for development of the mycelium. These  $\text{pH}$  values were also changed by the use of certain buffer salts. F. W. TANNER

Conditions affecting bactericidal power. E. A. COOPER, D. L. WOONHOUSE AND G. E. FORSTNER. *J. Soc. Chem. Ind.* 44, 134-8T (1925).—The unsatd. aliphatic acids are several times more efficacious as germicides than phenol. This activity is probably associated with the presence of the unsatd. linkage, as phenol is a more powerful disinfectant than cyclohexanol. For *B. coli* at 20° maleic acid is a more powerful germicide than fumaric acid, but at 37° the reverse is the case. This cannot be entirely explained by the relative acidity or affinity consists of the 2 acids. It would appear that the *cis*- and *trans*-type of stereoisomerism has some fundamental biological meaning. The nitroso compds. are in general very efficacious germicides in saline or broth, but their activity is considerably diminished in the presence of serum. Certain general principles correlating the chem. structure and bactericidal power of these compds. have been deduced from a systematic examn. of their germicidal action. The nitroso-anilines and dinitroso compds. are in particular very active germicides towards coliform organisms, being efficacious in concns. varying from 1 in 150,000 to 1 in 500,000. The usual methods for estg. germicidal power are not always suitable for accurately studying the influence of chem. constitution on bactericidal action, as the traces of org. matter introduced with the culture seriously affect the results. It is therefore essential to modify the technic either by suitable diln. of the culture or preferably by centrifuging in order to reduce the concn. of org. matter. The germicidal power of phenol and nitroso compds. is the same when detd. in physiol. salt soln. as in Ringer soln. (with  $\text{NaHCO}_3$  omitted). The presence of the bicarbonate sometimes seriously vitiates the

results, so that there is no advantage in employing Ringer soln. instead of isotonic salt soln. *B. coli communis* can acquire a tolerance to the action of nitroso compds.

F. W. TANNER

Hg derivatives of azo dyes (PROSKOURIAKOFF, RAIZISS) 10.

## D—BOTANY

B. M. DUGGAR

Organic synthesis in the vegetable world. MICHEL POLONOVSKI. *La nature* 53, i, 147-8(1925).—A general description. C. C. DAVIS

Investigations upon the presence of nickel and cobalt in plants. GABRIEL BERTRAND AND M. MOKRAGNATZ. *Bull. soc. chim* 37, 554-8(1925); cf. *C. A.* 19, 1020.—Small quantities of Ni and Co were found in a large no. of plants. H. R. KRAYBILL

The enzymes of *Utricularia vulgaris*. II. The relative content of proteoclastic enzymes in bladders and twigs. A. N. ADOVA. *Biochem. Z.* 153, 506-9(1924); cf. *C. A.* 19, 666.—Bladders and twigs of *Utricularia* were extd. with salt solns. The action of the ext. from bladders upon gelatin was found to be greater than that from twigs. Therefore, there is more protease in the bladders than in the twigs. Gelatin is best acted upon in alk. medium by the 100% ext. but with more dil. preps. it is best hydrolyzed when neutral. W. D. LANGLEY

The importance of maintaining certain differences between cell sap and external medium. W. J. V. OSTERHOUT. *J. Gen. Physiol.* 7, 561-4(1925).—"A striking difference exists between the internal and external soln. (sea water) of *Valonia macrophysa*. If this difference is abolished by placing cells in their own sap most of them quickly die. There is some ground for believing that the maintenance of differences between the sap and the external medium is of importance for vital processes. The sap of *V. macrophysa* is not a balanced soln. in the ordinary sense and the question may be raised whether in general the interior of the cell requires a balanced soln. in order to maintain life; or it may be that we must distinguish between internal and external balanced solns." CHAS. H. RICHARDSON

Contrasts in the cell sap of valonias and the problem of flotation. W. J. V. OSTERHOUT AND M. J. DORCAS. *J. Gen. Physiol.* 7, 633-40(1925).—*Valonia macrophysa* contains K and Na in the cell sap in the ratio of 5.72 to 1; in *V. renricosa*, which grows in a similar environment, the ratio is 0.0278 to 1. Other differences in the 2 species occur. Because of these differences, *renricosa* floats in sea water while *macrophysa* sinks. C. H. RICHARDSON

Influence of urea, thiourea and allylthiourea upon the higher plants. E. NICOLAS AND G. NICOLAS. *Compt. rend.* 180, 1286-9(1925).—The above named compds. which are represented by the formulas  $H_2NCONH_2$ ,  $H_2NCSNH_2$  and  $H_2NCSNH(C_2H_5)$ , resp., were tested with plants of white mustard and bean. The concns. employed were 0.2, 0.5, 1, 2.5 and 5 per 1000 of the nutrient soln. Urea was toxic in amts. greater than 1 in 1000. Thiourea and allylthiourea were toxic in quantities as small as 0.02 per 1000. L. W. RIGGS

Combined action of hydrochloric acid and metallic sodium on the reddening of a flavone extracted from red leaves of *Prunus pissardi*. ST. JONESCO. *Compt. rend.* 180, 1361-3(1925).—The autumnal red leaves of *Prunus pissardi* were dried and powdered, then were extd. for months with  $Et_2O$ . Among the many substances extd. was a yellow pigment, which after purification appeared as a tasteless, bright yellow powder, insol. in cold water, slightly sol. in boiling water from which soln. the powder was pptd. on cooling. It is insol. in dil. acids and but slightly sol. in concd. HCl. In concd.  $H_2SO_4$  it forms a soln. having a strong blue-green fluorescence. It dissolves in alkalis and is very sol. in MeOH, EtOH and  $Et_2O$ . In all of these properties it resembles the flavonic substances, particularly quercitine and its derivs. An alc. soln. of the freshly prepd. substance when treated with Na amalgam in the presence of HCl gives a red soln., which is not given with Zn and HCl, nor is it produced by Na amalgam alone when added to the alc. soln. Action of mineral and organic acids combined with that of metallic sodium upon the reddening of certain flavones. *Ibid.* 1523-5.—After the pigment was treated with Na, the addn. of  $H_2SO_4$  gave a more intense and persistent red coloration than with HCl.  $HNO_3$  gave a less intense red which rapidly changed to yellow. AcOH gave a pale red which disappeared in less than 1 min. By analogy from the reactions of quercitine the Na and nascent H convert the substance to a colorless pseudo-base which the HCl changes to a red pigment. Nascent H does not reduce the flavones to a red pigment. Metallic Na is the sole agent for the modification of the flavonic chromogens. The reddening is due to the action of HCl or  $H_2SO_4$  upon

the flavone modified by Na The red product thus obtained is not an anthocyanin.

L. W. RIGGS

Datiscin (datiscoside), a glucoside of *Datisca cannabina* L., and its products of hydrolysis. C. CHARAUX. *Compt rend* 180, 1419-21 (1923).—The root of *Datisca cannabina* collected after the fall of the leaves furnishes 10.5 g. of crude datiscin per 100 g. of dried root and the leaves furnish 6 g. per 100 g. of dried material. By recrystn. of the drug from boiling water and alc the purified product, m. 192-193°. It contains 10.8% of water and is *l*-rotatory,  $\alpha_D -48.59$  for the anhyd. product. Hydrolysis by 5%  $H_2SO_4$  on the boiling water bath gives 47.98% of anhyd. datiscetin and 55.6% of reducing sugar expressed as glucose. The hydrolysis of datiscin,  $C_{27}H_{36}O_{11}$ , by acids yields 1 mol. datiscetin, m. 272-273°, 1 mol. glucose and 1 mol. rhamnose. These sugars have been obtained in the cryst. form. By fermentative hydrolysis 1 mol. datiscin gives 1 mol. datiscetin and 1 mol. of rhamnoglucose identical with rutinose obtained from the fermentation of rutin.

L. W. RIGGS

Primeverose, the primeverosides and the primeverosidase. MARC BRIDEL. *Compt rend* 180, 1421-3 (1925), cf. *C. A.* 19, 2103.—From 18 kg. of fresh roots of *Primula officinalis* Jacq., 20 g. of a cryst. mixt. of primeverine and primulaverine were extd. A fermentative hydrolysis of this mixt. yielded primeverose which is identical to xyloglucose extd. from gentiacauleside, monotropitoside and from rhamnucoside. The reducing power of these glucosides is 0.646 to 0.648 of that of glucose and not 0.590 as calcd. by Goris, Mascré and Vischnac. The name *primeverosides* is proposed as a generic term to include the 5 cryst. glucosides which yield primeverose upon fermentative hydrolysis. Three of these primeverosides possess similar constitutions, thus monotropitoside yields on hydrolysis Me salicylate; primeveroside and primulaveroside are isomers and yield Me methoxysalicylate, the first giving the *m*- and the second the *p*-compd. In the 2 remaining primeverosides the products combined with primeverose are different, gentiacauleside from gentiacauleside is a flavonic deriv., and rhamnucoside from rhamnucoside is a pentahydroxymethylanthrol. The term primeverase should mean the enzyme of primeverose which yields xylose and glucose; it is not yet known to exist in the vegetable kingdom. *Primeverosidase* should designate the enzyme of the *l* rotatory primeverosides derived from  $\beta$  primeverose; it has been found in several species of plants.

L. W. RIGGS

## E—NUTRITION

PHILIP B. HAWK

The colloid chemistry of vitamin problems. F. V. VON HAHN. *Kolloid-Z.* 36, 271-4 (1925).—Of the 5 vitamins, A, B, C, D, and E, B and C may not be separable. They (B and C) are collectively called water-sol. vitamins. The surface tensions of water exts. of foodstuffs decrease in proportion to the water-sol. vitamin content of the food extd. A table of 51 foods is given. When foods are so treated that the water-sol. vitamin content is low the surface activity also becomes low. Potatoes show surface activities of (1) 24.3, of (2) 14.6 and of (3) 9.2 as the large vitamin content decreases from (1) raw potatoes, through (2) cooked or slow dried potatoes to (3) evapd. potatoes. All of Funk's solns. which contain vitamins are surface-active (about 25%). Those which do not contain vitamins show but little surface activity (2-4%). A collodion filter will hold colored materials of blood until surface-active substances are added; then it becomes permeable to the hemoglobin. Animal membranes behave in a similar manner. Vitamins are not definite chem. compounds, but are any substances which promote permeability of membranes, surface activity, and molecular dispersion. When such substances are present in concns. too small, some substances cannot get through the membranes into the blood stream and their deficiency causes disease. Vitamin substitutes have been used successfully. Experimental data will be published later.

F. R. BROWN

Action of adrenaline on metabolism during feeding and fasting. V. SUSANNA. *Folia Med* 1, (1922); *Arch. ital. biol.* 73, 152 (1924).—Adrenaline lessens, rather than accelerates metabolism; the effect (reduction of excretion of N and salts) is more marked in fasting animals.

A. T. CAMERON

Substances of incomplete vitamin action. M. PANTALEONI. *Polunin*, 29, 1653 (1922), *Arch. ital. biol.* 73, 149 (1924).—Certain substances, as spured rye, and  $NH_4$  lead to the disappearance of some avitamin symptoms in polyneuritic pigeons, while rice bran and beer yeast cause their complete disappearance.  $(NH_4)_2CO_3$ , urea, and ordonine are without action. Seeds of common fodder produce an effect only during germination.

A. T. CAMERON

Digestion trials with swine. II. Comparative digestibility of dry-fed maize, soaked maize, cooked maize and flaked maize. H. E. WOODMAN. *J. Agr. Sci.* 15, 1-18(1925); cf. *C. A.* 19, 531. III. Digestibility of a coarse grade of middlings. *Ibid* 19-21. IV. Utilization of whole milk by swine. *Ibid* 22-5 E. J. C.

Observations on the activity of vitamins. HANS V. EULER AND HARRY WIDELL. *Arkiv. Kems Mineral. Geol* 9, No 15, 1-5(1924).—The vitamin A content of the fats studied, as detd. by expts on rats, is unaffected by treatment for 1-2 days with 0.002 g. I per cc. of fat but it is appreciably lessened by 0.01 g of I and completely destroyed by 0.05 g I for the same amt of fat. A diet contg no antiophthalmic factor but contg irradiated lemon juice had little effect on growth but possessed a remarkable effect on bone formation. The authors conclude on the basis of expts reported elsewhere that not only the min quantity of vitamin is essential for metabolism but that the relative amts. of the different vitamins in excess of this play an essential role in the normal development of growing animals H. J. DEUEL, JR.

The metabolism of galactose. II. Blood sugar curves. A W. ROWE AND JOS. CHANDLER. *Endocrinology* 8, 803-31(1924), cf. *C. A.* 18, 3410.—The threshold tolerance for galactose averages 40 g in women and 30 g in men, the higher tolerance of the former being presumably due to the mammary gland. In certain patients in whom an increased tolerance is observed, it is not caused by a decreased rate of absorption since urea given with galactose to these patients is excreted in the urine at a normal rate. No relationship was found between the degree of hyperglucemia and the extent of the melaturia. R. and C. regard these as 2 wholly independent phenomena having a potentially common origin but being quantitatively mutually independent. A general relationship between the blood sugar curve and the size of the dose was observed, the larger the amt. administered the later in general before the peak of the curve was reached. H. J. DEUEL, JR.

The effective agent in the prevention or alleviation of the Chittenden-Underhill pellagra-like syndrome in dogs. F. P. UNDERHILL AND L. B. MENDEL. *U. S. Pub. Health Service, Pub. Health Repts.* 40, 1087-9(1925), cf. *C. A.* 11, 2099, 12, 288.—The pellagra like syndrome experimentally produced in dogs, which is clinically identical with "black tongue," a disease occurring spontaneously in these animals in an area analogous to that of pellagra in man, has been found to be associated with the lack of some unknown constituent in butter fat which is, however, not identical with vitamin A. The protective substance is also present to some extent in meat and in casein which has been boiled with alc. but whether the curative effect of these substances is caused by the protein or some substance of unknown compn associated therewith is unknown. The curative activity of butter has a seasonal variation and decreases with age. The extent of this curative action seems to be associated with the extent of pigmentation. Other substances rich in carotinoid pigments are particularly effective in alleviating the Chittenden-Underhill syndrome in dogs. U. and M. conclude that "we have adopted as a working hypothesis the possibility that the effective agent is either a natural pigmentary substance or some unidentified compd. associated therewith." H. J. DEUEL, JR.

Growth factors. III. HANS V. EULER, HENRY WIDELL AND ELSA ERIKSON. *Z. physiol. Chem.* 144, 123-31(1925); cf. *C. A.* 19, 1711.—A basal ration of 20% vitamin-free casein, 50% starch, 15% hardened peanut oil and 5% McCollum's salt mixt. was fed *ad libitum* to young white rats until an equl. in wt. was established. Then 1 g. of the substance to be tested was irradiated by a quartz-Hg lamp and administered daily. No further growth was obtained with irradiated  $H_2O$ , casein, hardened peanut oil or stearic acid, whereas growth was resumed by feeding irradiated peanut oil and oleic acid. The capacity for activation is probably a function of the unsatn. in the fatty acid. The  $CHCl_3$ -sol. pigment formed by treating cod-liver oil with concd.  $H_2SO_4$  and often considered a measure of vitamin potency is not obtained with activated peanut oil. The irradiated oil exhibits not only a growth-promoting power but also antirachitic and bactericidal activity probably associated with the  $Ca-PO_4$  exchange. IV. The influence of ID-excess on the growth of rats. H. V. EULER AND HENRY WIDELL. *Ibid* 132-6.—When rats are fed a large excess of cod-liver oil, the daily dose of C-vitamin (lemon juice) which is otherwise sufficient becomes insufficient for normal growth. Excessive feeding of cod-liver oil to the extent of 1000 times the normal requirement, with a corresponding reduction in the other fats of the ration, resulted in a large deposition of body fat. Without lemon juice the excess of ID led to a degeneration of osteoplasts in the epiphyses, whereas with copious administration of C the bone formation was normal. A. W. DOX.

Influence of a diet rich in calcium on the pathological symptoms of a dog after

partial parathyroid extirpation. H. H. JONKERS AND P. E. REYERS. *Z. physiol. Chem.* 144, 181-9(1925).—From a 20.2-kg. dog 3 epithelial bodies were removed. The blood Ca content, which before the operation was 6.4 mg. per 100 cc., rapidly diminished and in 6 days fell to  $\frac{1}{2}$ . Increase in muscle tonus and reflex excitability was followed by distinct tetany symptoms. Feeding of Ca (bones) then caused a rapid rise in blood Ca, the pathological symptoms disappeared, but the muscle tonus and reflex remained above normal. 1.5 l. of milk and bread did not supply sufficient Ca to prevent the occurrence of convulsions. Muscular work increased the tendency to convulsions. Even after 7 months of the Ca rich diet no compensation of epithelial function had resulted, since a reduction of the Ca in the diet brought back the convulsions. Injection of 10 cc of 5%  $\text{CaCl}_2$  rapidly restored the animal. A disturbance in the mineral metabolism appears to be the cause of the phenomena observed after parathyroid extirpation.

A. W. DOX

Sufficiency of fat in sailor's diet. BELLE. *J. méd. Bordeaux* 14, 603(1924); *Physiol. Abstracts* 9, 527.—A definite quantity of fat is essential in a sailor's diet, and no amt. of carbohydrate can replace even part of this. Deficiency in this respect is a factor in the premature senility so common in sailors.

H. G.

The alimentary factor in tuberculosis. MOURQUAND, ROCHAIX, MICHEL AND BERTOYE. *J. méd. Bordeaux* 14, 622(1924); *Physiol. Abstracts* 9, 530.—Expts. on guinea pigs, in which the animals' constitutions were modified by special diet, and tuberculous infection in these took a different course from that in the normally fed animals. H. G.

Metabolic experiments on rats and digestibility of the proteins of some foodstuffs. B. C. P. JANSEN AND W. F. DONATH. *Meded. Burgerl. Geneesk. Dienst Nederland. Indie* 1924, 24-45; *Expt. Sta. Record* 52, 63.—A series of metabolism expts. conducted on rats to det. the digestibility of the proteins of some foodstuffs in common use in the Dutch East Indies is reported, together with a description of a metabolism cage devised by the authors. The digestibility of the protein of the various foods tested was calcd. in 2 ways  $\text{N-urine}/\text{N-food} \times 100$  or digestive factor A, and  $(\text{N-food}-\text{N-feces})/\text{N food} \times 100$  or digestive factor B. In general, daily detns. were made for from 8 to 14 days. In the tests with rice, the rice was used as the sole food, and in the tests with soy beans and chayote leaves these were fed with cassava meal and coconut oil. The digestive factors A and B and the N balance in mg. for the different foods tested are, resp., as follows: unpolished rice (N content 1.2%) 60.2, 63.2, and +9.2; polished rice (N content 1.05%) 72.7, 70.3, and -4.7; polished rice to which bran ext. had been added (N content of the mixt. 1.2%) 73.5, 66.3, and -16.5; polished rice (N content 1.05%) 73.6, 77.3, and +17; half-polished rice 100 years old (N content 1.27%) 78.1, 78.7, and -19.8; polished rice (N content 1.19%) 83.7, 84, and +3.8; soy bean (N content of the mixt. 3.79%) 73.3, 76.4, and +58.8, and chayote leaves (N content of the mixt. 2.65%) 80.4, 67.1, and +83. For comparison with the rat expts., 3 metabolism expts. were conducted on human subjects, with rice as the chief source of N. In the expt. in which half-polished rice with a N content of 1.3% was used, the values for digestive factors A and B were 67 and 64.5%, with a N balance of 0.43 mg. Corresponding values for unpolished rice with a N content of 1.2% were 54.7, 47, and +1.04 and for the half-polished rice 100 years old 65, 65, and +0.08.

H. G.

The vitamin A content of different Indian foodstuffs and the value of the proteins of the latter as a supplement to the proteins of rice. B. C. P. JANSEN AND W. F. DONATH. *Meded. Burgerl. Geneesk. Dienst Nederland. Indie* 1924, 46-98; *Expt. Sta. Record* 52, 64-5.—Foods in common use in the East Indies were tested for their value as sources of proteins and vitamin A by being fed to rats as supplements to a diet of polished rice. In general the curative method was used, i. e., the food to be tested was not added to the ration until the animals had ceased growing and in many cases had developed xerophthalmia. To det. whether failure to grow was due to protein or vitamin deficiency, cod liver oil was added to all diets in which growth had ceased. From the results reported, a classification of the various foodstuffs with respect to vitamin A has been made along the lines noted in a study of vitamin B (C. A. 18, 1691): (1) Foodstuffs very rich in vitamin A, of which the addn. of from 1 to 5% on the dry basis is sufficient to supplement satisfactorily a vitamin-A-free basal diet. Among the food materials placed in this group, with the estd. amts. for curing xerophthalmia, are the following fruits: banana 0.5, sapodilla 1, papaya 1, and avocado from 0.5 to 1 g. The vegetables included in this group are cowpeas (dried and powd.) 3, leaves of cowpeas dried 3, cassava leaves (boiled and dried) 5, pumpkin leaves (boiled and dried) 1, fresh pumpkin from 1 to 2, boiled and dried pumpkin 5%, chayote fruit or leaves (boiled and dried) 5, and fresh cucumber from 5 to 10 g. Animal products in this group include ducks' eggs (dried and sealed) 3, butter preserved in tins 5, and cod-liver oil

0.5%. (2) Foodstuffs having so little vitamin A as to be insufficient to prevent the symptoms of vitamin A deficiency when used exclusively. In this group are placed rice (polished and unpolished), corn (at least the white variety), coconut press cake, and peanut press cake. (3) Food materials which do not furnish sufficient vitamin A when fed at a level of from 5 to 10%, but might prove sufficient if given in larger amts. In this group are placed meat, soy beans, dried fish and shrimps, and palm oil. Definite conclusions are not drawn concerning the protein values of the foods tested, although it is considered that the proteins of soy beans are of greater value than those of meat or dried fish. Materials recommended as best fitted to supplement the deficiencies of rice in vitamin A are bananas, fresh or boiled vegetables, and ducks' eggs. It is estd. that the use of 1 banana daily is sufficient to prevent symptoms of vitamin A deficiency on a diet consisting chiefly of rice. H. G.

**Storage of vitamins.** H. ARON AND R. GRALKA. *Klin. Wochschr.* 4, 820-1 (1925).—Fat-sol. A is stored; water-sol. B is not stored. MILTON HANKE

**Determination of the growth-promoting activity of vitamin B.** HANS ABELS. *Klin. Wochschr.* 4, 1314-5 (1925).—Pigeons are fed for 1 week on a diet deficient in vitamin B. The feathers are then plucked from 1 breast. They will not regenerate on a diet deficient in B but they will regenerate if B is supplied. The speed of regeneration is directly proportional to the amt. of B that is supplied. MILTON HANKE

**Effect of vitamin B deficiency on reproduction.** A. S. PARKES AND J. C. DRUMMOND. *Proc. Roy. Soc. (London)* 98B, 147-71 (1925).—Degeneration of the testes and sterility result in a short time when a buck rat is placed on a ration totally deficient in vitamin B. If the ration be only partially deficient in this vitamin, this result is postponed temporarily or indefinitely. After the degeneration has become severe, a normal diet restores the vigor and body wt. of the animal, but does not restore the testes to normal. The degree of degeneration of the testes is a function of the degree of deficiency of vitamin B in the ration and of the period of feeding of the deficient ration. The fecundating power of the buck is greatly depleted before sterility occurs. The size of the litter varies but little. The proportion of males among the young decreases with both the degree of deficiency and the period of feeding of the deficient ration.

**Experimental investigations of the carbon excretion in normal urine, in avitaminosis, in the undernourished and in hunger.** K. SCHMIZU. *Biochem. Z.* 153, 424-55 (1924).—Dogs were kept upon different diets and the excretion of urinary N and C was detd. Upon a normal and sufficient diet, the ratio C/N (i. e., C excreted to N excreted) was practically const. With increase of carbohydrate in the food, the ratio increased. Some of the C excreted is in the form of N-free substances which are not acetone bodies. During starvation, both C and N decreased, and then N increased more than C. Before death N again increased out of proportion to C. During avitaminosis C/N increased, not because of incomplete oxidation of nitrogenous substances, but perhaps because of incomplete oxidation of carbohydrates or fats. W. D. LANGLEY

**The new dietetic treatments for diabetes.** L. R. GROTE. *Centr. Inn. Med.* 45, 3-12 (1924).—Three cases each of severe diabetes are treated with the starvation method of Allen and the high fat diet of Petren. The results seem to have been better with the high fat diet. In the Allen treatment the extreme starvation produces hunger-edema and an injury to the body cells and tissues which is slow to disappear. J. H. I.

**Fats and lipoids of the blood. II. Distribution of fat and lipid in the blood of rabbits on diets lacking vitamin B.** RYUZO IWATSURU. *Arch. ges. Physiol. (Pflüger's)* 208, 41-8 (1925); cf. C. A. 18, 1525.—The fat in the blood of rabbits fed upon a vitamin-free (B) diet becomes reduced, just as is the case with pigeons upon a rice diet. In starving rabbits and in those with a B avitaminosis the fat and lipid values of the red blood cells differ but little from normal. This is also true for the different lipid fractions of the blood cells. Conditions in the blood serum in B avitaminosis are interesting, in that the amts. of fat and lipid are increased to a considerable degree. Cholesterols are usually increased about 3-fold; the lecithins and the total fatty acids about 1.5 times. In the later stages of the disturbance a considerable reduction occurs. The ester fraction of the serum cholesterol is more markedly increased than is the total cholesterol. In the relative values for the distribution of fats and lipoids no differences could be detected between the conditions noted in avitaminosis and those found in starvation. G. H. S.

**Quantitative determination of vitamin A.** H. C. SHERMAN AND H. E. MUNSELL. *J. Am. Chem. Soc.* 47, 1639-46 (1925).—For the detn. of the relative vitamin A content of foods, it is recommended that albino rats of known nutritional history be placed, when 28-29 days of age, upon a diet adequate in all other respects but free from vitamin

A. After growth has ceased, the young rats nec to be kept in individual cages and at least 1 of each litter should be continued on the basal diet free from vitamin A until death, as a "negative control," while the others are to be fed graded portions of the food to be tested, as their sole source of vitamin A, daily or at other suitable intervals, during a test period of 8 weeks. By sufficient repetitions, the min allowance of food which will induce an av. gain in wt. of 3 g per week during the test period can thus be ascertained. The unit recommended for numerical expression of results is that amt. of vitamin A which, when fed daily, induces an av. gain of 3 g per week in a standard test animal under the conditions described. The choice and control of the basal diet, of the test animals and of the exptl. procedure, and the interpretation of the findings, are discussed. C. J. WEST

Quantitative experiments upon the occurrence and distribution of vitamin A in the body and the influence of the food. H. C. SHERMAN AND L. C. BOYNTON. *J. Am. Chem. Soc.* 47, 1646-53(1925).—The distribution of vitamin A in the body of the rat was studied by feeding the tissues of adult animals, as the sole source of this vitamin, to young rats which had ceased to grow on a diet otherwise adequate. An av. of all directly comparable results on adult rats reared on a diet of  $\frac{1}{2}$  whole milk powder and  $\frac{1}{2}$  whole wheat showed the kidney to be at least 40 times as rich as the muscle, the lung more than 40 times and the liver from 200 to 400 times as rich in vitamin A per g. as muscle. The vitamin A content of the food influenced that of the body. That the difference in the amt. of vitamin A found in the liver and in the lung tissue was directly attributable to the different amts. of this vitamin in the food was further shown by a comparison of the tissues of 10 weeks old rats that had received addns. of cod liver oil to the basal diet with tissues of rats of the same age and diet without cod-liver oil. C. J. WEST

Bodily storage of vitamin A as influenced by age and other conditions. H. C. SHERMAN AND L. B. STORMS. *J. Am. Chem. Soc.* 47, 1653-7(1925).—Among animals coming from the same previous diet, age has an important influence upon the length of the survival period upon food devoid of vitamin A. The max. survival period, and, therefore, presumably the max. body store of vitamin A (or at least the max. store in relation to daily need) is at 6 months of age, or about at the beginning of full adult life. A moderate difference in the vitamin A content of the food causes a marked difference in the amt. of this vitamin stored in the body as indicated by the survival period on food free from vitamin A. The incidence of the characteristic symptoms as influenced by the age at which the exptl. animal is subjected to vitamin deficiency is discussed briefly. C. J. WEST

Relation of vitamin A to growth, reproduction and longevity. H. C. SHERMAN AND F. L. MACLEON. *J. Am. Chem. Soc.* 47, 1658-62(1925).—Parallel groups of rats of identical previous history were fed upon 2 types of diets, 1 rather low and the other fairly high in vitamin A, from soon after weaning time until natural death. The smaller quantity of vitamin A proved sufficient for normal growth, up to nearly av. adult size but not for successful reproduction and rarely did it support satisfactory longevity. The parallel animals receiving the more liberal allowance of vitamin A grew to fully av. adult size, were successful in reproduction and the rearing of young and lived on the av. over twice as long as those on the diet equally good in all other respects but lower in vitamin A. These expts show that a proportion of vitamin A in the food sufficient to support normal growth and maintain every appearance of good health, for a long time at least, may still be insufficient to meet the added nutritive demands of successful reproduction and lactation. Along with the failure to reproduce successfully there usually also appeared in early adult life an increased susceptibility to infection and particularly a tendency to break down with lung disease at an age corresponding to that at which pulmonary tuberculosis so often develops in young men and women. The bacillus involved is different; but the close parallelism of increased susceptibility of the lung to infection at this stage of the life history appears very significant, especially in view of the fact recorded (preceding abstr.) that the vitamin A content of lung tissue varies with that of the food. Vitamin A is an even more important factor in the chemistry of food and nutrition than has previously been appreciated. C. J. WEST

Further studies on the effect of iodides on the human nitrogen metabolism. G. P. GRABFIELD AND A. M. PRENTISS. *J. Pharmacol.* 25, 411-21(1925); cf. *C. A.* 18, 1324.—The exhibition of Na, Li, Ca, K, Sr and Mg iodides, Lugol's soln. and "sajodin" increases the urinary N excretion of subjects in positive N balance on a const. protein intake. When Na, Li, Sr or Mg iodides are exhibited the increase in N output is immediate. When  $\text{CaI}_2$  or  $\text{KI}$  is given the increase in N output is delayed; in these expts it occurred after the 3-day period of drug administration. Changes in the non-protein

N of the blood correspond to urinary changes, i. e., falling if the urinary output is immediate and rising until the increased excretion begins when the latter is delayed.  
C. J. WEST

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## F—PHYSIOLOGY

ANDREW HUNTER

The nature of the process of transformation of creatine into creatinine in the organism. R. ANDÒ. *Arch. fisiol.* 20, 225-35(1922); *Arch. ital. biol.* 74, 154(1924).—Creatinine appears during autolysis in tissues that contain creatine. It is formed in the absence of all enzyme action, with reduction of the original amt. of creatine. This is considered due to developing acidity.  
A. T. CAMERON

The carbohydrate metabolism of the human placenta. K. FELIX AND KJ. VON OETTINGEN. *Z. physiol. Chem.* 144, 190-5(1925).—Immediately after ejection the fresh placenta contains only 0.1-0.2% glycogen and after 2 hrs. the amt. decreases to 0.03%. Perfusion of the placenta with defibrinated blood to which Ringer soln. and glucose had been added gave no increase in glycogen. However, 18-38% of the glucose disappeared during a 45 min. expt. On the other hand, when glucose and insulin were added to the perfusion liquid an increase in glucose (Bertrand detn.) was noted but no corresponding decrease in glycogen. Probably the glucose is transformed through the influence of insulin into simpler substances with greater reducing power. Such a process would represent an oxidation. Addn. of KCN to inhibit oxidation suppressed the insulin effect, and a decrease in reducing sugar occurred as before. A similar result was obtained with glucose and KCN without insulin.  
A. W. DOX

The formation of lactic acid and of phosphoric acid in the gland. ERNST SCHMITZ AND FRIEDRICH CHROMETZKA. *Z. physiol. Chem.* 144, 196-218(1925).—Attempts were made to det. whether the energy of glandular activity is supplied by carbohydrate via cleavage of hexose-diphosphate into  $H_2PO_4$  and lactic acid, as is the case with muscular activity. The glands studied were the submaxillary and parotid of the horse, the expts. being performed with fresh pulp or press juice. During 1.5 hrs. at 40° both lactic acid and  $H_2PO_4$  are liberated but not in const. proportions. In only 20% of the expts. did the proportions deviate less than 10% from the calcd. ratio. Addn. of fructose phosphate gave an increase in  $H_2PO_4$  but not in lactic acid. Increase in  $H_2PO_4$  resulted also from addn. of nucleic acids. No evidence was obtained of the presence of a lactacidogen-splitting enzyme, and the  $H_2PO_4$  appears to arise mainly from other sources. With the salivary glands chem. processes rather than energy production predominate, and it is not surprising that the utilization of carbohydrate occurs in some other manner than in the muscle, perhaps in the same manner as in the liver.  
A. W. DOX

The mathematical rule of regularity in the change of colostrum into milk. W. GRUBER. *Milchwirtschaft. Forsch.* 2, 31-46(1924).—The change from colostrum to milk may be represented by a logarithmic curve and this change is a transcendental function of the time. The decrease in the individual constituents in the change from colostrum to milk is proportional to the difference between the amt. of these substances present at a given time and the minimum amts. at the end of the colostrum period. This law holds best for the solids not-fat, N, and serum protein, while the values for the fat, lactose and partly also the casein do not follow this law or agree with the curve. After the change from colostrum to milk the curve no longer holds. A number of tables and curves are given.  
O. L. EVENSON

The chemical and physical constants of colostrum fat. HEINZ ENGEL, HANNA SCHLAG AND WALTER MOHR. *Milchwirtschaft. Forsch.* 2, 47-56(1924).—The change in the physical and chem. const. of the colostrum fat from 6 cows during the colostrum period is shown by means of tables and curves. In general the Polenske, Reichert-Meißl and sapon. nos. rise while the iodine no., solidification point,  $n$  and m. p. fall rapidly at the beginning of the period and slowly towards the end.  
O. L. E.

Action of pilocarpine, thirst and vagal block on gastric secretion in dogs. G. AMANTEA. *Arch. fisiol.* 22, 211-28(1924); *Physiol. Abstracts* 9, 523.—The exciting action of pilocarpine on gastric secretion is confirmed. Thirst causes a diminution of the quantity of gastric juice secreted and a slight increase in its acidity. The temporary suppression of the function of both vagi, whether obtained by means of stavaine or electrically, considerably diminishes, but does not entirely stop gastric secretion. This returns to the normal about 2 hrs. after the removal of the block.  
H. G.

**Variations in the resistance of red blood corpuscles in physical work.** L. v. LIEBERMANN AND D. ACÉL. *Z. Hyg. Infektionskrankh.* 99, 67-75(1923); *Physiol. Abstracts* 8, 330.—Hard phys. work decreases the resistance of red blood corpuscles exposed to hypertonic salt solns. in the beginning, but later on it increases it considerably. This increase is due to the destruction of the less resistant red blood corpuscles. The decrease of resistance preceding the increase may partly be ascribed to an increased formation of  $\text{CO}_2$  or of some fatigue products (e. g., lactic acid). H. G.

**The blood supply to the pancreas with some perfusion studies.** WM. S. COLLENS. *J. Biol. Chem.* 64, 461-72(1925).—Injection of the pancreas and duodenum of dogs through the thoracic aorta showed that the hepatic arteries and the superior pancreaticoduodenal artery arise from the gastroduodenal artery and that there are, within both duodenum and pancreas, anastomoses between the superior and inferior pancreaticoduodenal arteries. Repetition of the work of Epstein and Rosenthal (*C. A.* 19, 674, 1894) confirmed their results but, when the superior pancreaticoduodenal artery or the hepatic arteries were tied, there was no hyperglucemia nor glucosuria. Perfusion of the hepatic arteries alone led to hyperglucemia and glucosuria. The conclusions of E. and R. are, therefore, unjustified. I. GREENWALD

**Further studies on the physiological action of a parathyroid hormone.** J. B. COLLIP AND E. P. CLARK. *J. Biol. Chem.* 64, 485-507(1925); cf. *C. A.* 19, 2070, 2077.—Although there is considerable difference in the effect exerted upon different dogs, a variation which may be associated with previous diet, a unit of potency has been provisionally defined as 0.01 of the amt. which will produce an av. increase of 5 mg. in the blood serum Ca of normal meat-fed dogs of approx. 20 kg. over a period of 15 hrs. Up to an increase of 6 or 7 mg. the increase is proportional to the amt. injected. No single injection, no matter how large, has proved fatal. A high content of Ca in the serum does not cause any untoward symptoms but, if it be maintained by repeated injections, toxic symptoms and death ensue. Vomiting is the first symptom but dogs may recover after vomiting, if the injections are discontinued. Injection of hypertonic solns. of glucose or of NaCl deferred death in animals receiving repeated injections. The concn. of Cl in the blood was sometimes initially increased but was, more frequently, finally decreased. Blood phosphate showed little change until after the Ca had reached its max. value, about 20 mg. per 100 cc. serum, but as death approached rose rapidly to as much as 18 mg. per 100 cc. blood. The increase in serum Ca could be obtained even under amytal anesthesia. The ext. was as active upon parathyroidectomized as upon normal dogs. Administration of ext. and guanidine to the same dogs was followed by hypercalcemia and tetany. Rabbits are rather resistant to the action of the ext. I. GREENWALD

**Effect of temperature on the blood sugar concentration.** E. GEIGER. *Klin. Wochschr.* 4, 1265-8(1925).—Lowering the outside temp. has no effect upon the blood sugar concn. if the body temp. is not lowered. A reduction in the body temp. is associated with hyperglucemia. Toxic fever (artificially induced) is associated with a hyperglucemia. When the fever subsides naturally, a hypoglucemia occurs. If the fever is reduced with antipyretics, the hyperglucemia increases regardless of the nature of the antipyretic. When sufficient antipyretic is given to reduce the normal body temp., a hyperglucemia is obtained that varies directly with the fall in body temp. MILTON HANKE

**Clinical observation and study of the endocrinology involved in phosphorus and calcium metabolism.** R. F. KNOLL. *J. Am. Inst. Homeopathy* 18, 584-98(1925).—A discussion of the influence of the thyroid, parathyroids, thymus, pituitary and gonads on the metabolism of Ca and P. JOSEPH S. HEPBURN

**Biological action of light.** D. T. HARRIS. *Proc. Roy. Soc. (London)* 98B, 171-87(1925).—Ultra-violet radiations exert a stimulant action on the gaseous metabolism of the rat and on the movements of the isolated frog stomach. The latter phenomenon is due to physiol. antagonism, not to phys. interference. The decrease in heat production, which occurs when an animal is exposed to the mixed radiations of a powerful source of light, is greater in pigmented animals than in albinos for the same increase in temp. in the surrounding medium. Pigment, under these conditions, apparently is a factor in decreasing heat production. Thermoelec. measurements demonstrate that pigment has high absorptive properties. The absorbed radiant energy is converted into heat and produces an appreciable increase in temp. in the dermis. Pigment apparently protects an animal against the lethal action of certain photodynamic substances. JOSEPH S. HEPBURN

**Effect of exercise on sugar and residual nitrogen in blood.** CÉSAR AND SCHAAL. *Z. klin. Med.* 98, 96-9(1924); *J. Chem. Soc.* 126, 1, 1123.—From 20 to 46 min. after par-

ticipation in a foot race, the sugar content of the blood was more than doubled, while its residual N was not markedly affected. JOSEPH S. HEPBURN.

The regulation of blood sugar and of the reaction of the blood in man. II. The physicochemical regulation of respiration in hypoglycemia. G. ENDRES AND H. LUCKE. *Z. ges. expil. Med.* 45, 283-95 (1925); cf. *C. A.* 19, 2235.—In healthy individuals a change in the regulation of blood sugar by insulin is not paralleled by a physicochem. regulation of respiration. Subcutaneous and intravenous insulin injections cause a marked lowering of blood sugar content but no disturbance of the acid-base equil. of the blood and the actual reaction of the blood remains unchanged. At the time when hypoglycemia is most pronounced, the percentage of N and  $\text{NH}_3$  content of the urine is lessened and in half of the cases there is a decrease in the acidity of the urine, but the alveolar  $\text{CO}_2$  tension remains unchanged. In animals treated with insulin there is an increased production of lactic acid which was not noted in these observations on healthy men. HARRIET F. HOLMES.

Corpus luteum extracts and ovulation in the rabbit. W. P. KENNEDY. *Quart. J. Exptl. Physiol.* 15, 103-12 (1925).—A substance can be extd. from the fresh or desiccated cow corpus luteum which inhibits ovulation in the rabbit when injected intravenously. Long-continued dosage may be correlated with degenerative changes in the ovary, also in the liver and adrenal glands but of lesser degree. Ability to ovulate was not recovered within three months after treatment. Fertility of the male was not affected. FRANCES KRASNOW.

The significance of the elastic tissue of the human fetus. EVELYN E. HEWER. *Quart. J. Exptl. Physiol.* 15, 113-7 (1925).—Elastic tissue appears early and is widely distributed. Its appearance is often correlated with the time at which functioning of the organ begins. FRANCES KRASNOW.

The action of pituitary extract on urinary secretion. N. S. CRAIG. *Quart. J. Exptl. Physiol.* 15, 119-54 (1925).—Intravenous administration of pituitary ext. to anesthetized animals produces definite diuresis. Subcutaneous injection of ext. in dogs controls the diuresis that would normally result from the administration of water or physiological saline soln. by mouth. If coned saline soln. is used diuresis results. Drinking large quantities of water immediately preceding a subcutaneous injection of ext. causes a definite reduction in the hemoglobin during the 1st 2 hrs. in man. FRANCES KRASNOW.

Studies on the pituitary. V. The avine depressor response. L. T. HOGGEN. *Quart. J. Exptl. Physiol.* 15, 155-61 (1925); cf. *C. A.* 19, 1031.—"The substance present in pituitary exts. causing a powerful depressor response in the bird is a sp. property of the fresh gland substance: it does not belong to the category of capillary poisons common to exts. of many tissues, and in particular has no connection with the histamine-like substance responsible for the secondary fall in carnivora ... " It is sol. in water, in alc., and is stable at the b. p. of water and readily inactivated by trypsin and alkali. VI. Localization and phyletic distribution of active materials. L. T. HOGGEN AND G. R. DE BEER. *Ibid.* 163-76.—"The oxytocic and avine depressor responses are given with exts. of the pituitary of mammals, birds, reptiles, amphibians, bony and cartilaginous fishes." The activity of the exts. of the elasmobranch pituitary is in both respects small compared with that of exts. of the teleost. The pars intermedia have a higher oxytocic than pressor activity. FRANCES KRASNOW.

The action of pituitary extracts on intestinal muscle. A. D. MACDONALD. *Quart. J. Exptl. Physiol.* 15, 191-200 (1925).—Pituitary exts. vary greatly in their content of intestinal stimulant. This differs from other known pituitary principles in being alc. sol. and alkali stable. Lab. preps. do not act in consens. to which much physiol. significance can be attached. "The pituitary is not materially richer in the stimulant than several other tissues." FRANCES KRASNOW.

Researches on the vaso-constriction properties of blood serum. O. B. MEYER. *Z. Biol.* 82, 400-10 (1925).—Adrenaline is destroyed by heating for 1½ hrs. at 60°. The vaso-constriction action of blood serum is greatly decreased if heated at the same temp. for the same time. Such treatment injures the vaso-constriction power of histamine soln. only partly. Addn. of lactic acid to serum lowers markedly its vaso-constriction property. FRANCES KRASNOW.

Researches on the physiological closure of the umbilical cord arteries. WALTER RECH. *Z. Biol.* 82, 487-512 (1925).—Perfusion of the cord arteries with O satd. soln. called forth very strong contraction of the musculature. The contraction is so energetic that there is a constriction of the vessel lumen which is not opened by an increase in the perfusion pressure. This may explain the physiol. closure of the umbilical cord since such closure is very intimately connected with the onset of lung breathing. F. K.

A sinus hormone of the frog heart. L. HABERLANDT. *Z. Biol.* 82, 536-44(1925).—An ext. of the sinus is made with Ringer soln. It is shown that this specially affects the action of the heart, both the tone and rate of the pulse are increased. F. K.

Guanidine compounds among the extractives of the steer testes. HELMUT MÜLLER. *Z. Biol.* 82, 573-80(1925).—From the arginine fraction was obtained creatinine. The lysine fraction yielded choline. In the filtrate from the  $HgCl_2$  pptn. were found hypoxanthine (identified as the picrate) and lactic acid (identified as the Zn lactate). In a sep. portion of the original ext. were obtained dimethylguanidine as the chloroaurate,  $C_2H_5N_3$ ,  $HCl \cdot AuCl_4$  and methylguanidine as the chloroaurate,  $C_2H_5N_3$ ,  $HCl \cdot AuCl_4$ .

FRANCES KRASNOW

Studies on antagonistic nerves. XXVI. The hormone transmission of nerve action of the heart. KIMIO NAKAYAMA. *Z. Biol.* 82, 581-604(1925).—Proof is given to contradict the belief that a hormone controls the vagus action as interpreted by Loewis. XXVII. Calcium mobilization in the heart due to stimulation of the nervus accelerans. TERNICHI YASUTAKE. *Ibid.* 605-10.—Stimulation of the nervus accelerans (turtle) causes mobilization of Ca in the ventricle. The increase in Ca is greater than normal during perfusion with Ringer soln. K increase on vagus stimulation and Ca increase on sympathetic nerve stimulation are chem. changes which are as antagonistic as the stimulation of the nerves themselves.

FRANCES KRASNOW

Animal calorimetry. IV. The dynamic action of split proteins; the calculation of this action. J. MELLY AND A. V. RÖRTH. *Biochem. Z.* 153, 285-301(1924); cf. *C. A.* 19, 1444.—Dogs inactivated by injections of curare were placed in a thermostat at  $30^\circ$  and the gas exchange was detd. Erepton (a hydrolyzed meat prepn) was then injected, and the resulting variations in gas exchange were followed. From the respiratory quotient, the heat production per unit of body surface was found to vary; e g., on 4 successive days the values were 918, 871, 819 and 818 kg. cal. per sq. m. O consumption increased from 14 to 21%. The corresponding calcd. energy increase was 30.5-52.8%. The sp. dynamic action of erepton, as calcd. from 3 expts., is 16, 11 or  $8\frac{1}{4}$  with an av. value of 12.

W. D. LANGLEY

Lipoids of the thyroid and parathyroid. H. J. ARNDT. *Beitr. path. Anat.* 72, 517-79(1924).—In the glandular cells of the human thyroid and parathyroids, lipoids are generally found. Occasionally the parenchyma of the glands in question contains mixts. of true lipoids with either neutral fats or fatty acids, or both. The chem. characteristics of the lipoids of the thyroid and parathyroids are independent of the general nutrition, age and pathological affections of the subjects, although neutral fat occurs most frequently in young individuals. The lipoids of the parathyroids are already present in the 2nd yr. of age, and increase in quantity in subsequent yrs., reaching a max. in old subjects. The lipoids of the thyroid appear sooner than those of the parathyroid, and their quantity increases afterwards, though not as much as in the parathyroids. In the stroma of the parathyroids fat cells occur, the quantity of which is related to the general state of nutrition and age of the subjects, this may occasionally lead to a lipomatous pseudo-hypertrophy of the glands. Interstitial and, as a rule, subcapsular fat cells are seen also in the thyroid, but not regularly and independently of age. Double refracting lipoids (cholesterol esters) are observed only now and then in the stroma of the parathyroids and colloid of the thyroid, where also drops of neutral fat and fatty acids are found. The content in lipoids of the thyroid and parathyroid has no correlation with that of the adrenals. Independently of their chem. characteristics the lipoids of the thyroid and parathyroids increase in quantity as the amt. of glycogen present in these glands diminishes.

JULIAN H. LEWIS

Note on moisture-absorbing effects of carbon dioxide absorbents for metabolism experiments. ROBERT E. WILSON. *Bost. Med. Surg. J.* 187, 132-5(1922).—This meets a criticism of Roth (*C. A.* 16, 2703) who claims the failure of Wilson soda lime to absorb  $H_2O$  in basal metabolism expts. is a defect in this absorbent. W. claims that the moisture in his soda lime maintains a const. humidity of 80%, and the error made in correcting the vols. measured with the soda lime by using a correction table calcd. for 80% humidity is actually less than that made by using a caking absorbent and correcting on the customary assumption of 0% humidity.

JULIAN H. LEWIS

Conditions of activity in endocrine glands. XVI. The role of the adrenal medulla in pseudodiffuse hyperglucemia. T. BULATAO AND W. B. CANNON. *Am. J. Physiol.* 72, 295-313(1925).—Further evidence is given that medulladrenal secretion plays an important part in mobilizing sugar from the liver.

J. F. LYMAN

The causes of hemolysis. V. V. LEVINSKY. *Medd. Vetenskapskad. Nobelinst.* 6, No. 11, 1-26(1922); *Chem. Zentr.* 1924, II, 1940.—Hemolysis is envisaged as the decomposition of the hemoglobin-lipoid compds. which form the main component of the proto-

plasm of the corpuscles, the membrane of the corpuscle not entering into the process. It is therefore caused by any agent or process which tends to produce this decompos.; agitation or centrifuging may assist such processes. Most of such agents are those which attack (cause "Denaturierung" of) the hemoglobin, viz., elevated temps., acids, alkalis, heavy metal salts, etc. It may also be produced by substances which attack the lipoids, as saponin.

WM. B. PLUMMER

The production of carbon dioxide by nerve. G. H. PARKER. *J. Gen. Physiol.* 7, 641-69(1923).—CO<sub>2</sub> was detected by a modified Osterhout respiratory app. (cf. *C. A.* 13, 231) which is described. Lateral-line nerve from the dogfish discharges CO<sub>2</sub> violently for about 1/4 hr., then steadily at a lower rate for several hrs. Handling the nerve does not increase the CO<sub>2</sub> output, but cutting revives the initial high rate. This CO<sub>2</sub> is a true nervous metabolite. Its rate of discharge from quiescent nerve varied from 0.0071 to 0.0128 mg. per g. nerve per min., av. 0.0095 mg. The CO<sub>2</sub> production of stimulated nerve was 15.8% over that of quiescent nerve. This study indicates that chem. change is a factor in nerve stimulation.

C. H. RICHARDSON

Function of creatine in muscular contraction. O. W. TIGGS. *Australian J. Exptl. Biol. Med. Sci.* 2, 1-18(1925).—Frog muscles, fatigued and then immersed in Ringer fluid, liberate a substance into the surrounding fluid, which, on boiling with acid, yields creatinine. Although the creatine content of fresh muscle is but slightly less than that of fatigued muscle, the amt. of creatine liberated by fresh muscle is much less than that liberated by fatigued muscle. Fatigued muscles which have been subjected to a stream of O for 5 hrs. liberate very much less creatine than fatigued muscles placed for a similar period in a small vol. of air. Fatigued muscles liberate creatine and lactic acid in equiv. quantities. Muscle creatine probably has a cyclic structure  $\text{HN} = \text{C} \begin{array}{c} \diagup \text{N}-\text{CH}_3 \\ \diagdown \text{N}-\text{CH}_2\text{CO}_2\text{H} \end{array}$ .

It is inferred, that the change which the creatine undergoes during excitation is a splitting open of this ring, resulting in the formation of a free amino group, and that it is this substance which, being formed on the surface of the 1 excitable membrane, neutralizes the lactic acid produced on the other, and thereby causes muscular relaxation. During oxidative recovery it is reconverted into creatine. Urinary creatinine appears to be the anhydride of the basic creatine that is constantly leaking into the blood; the rise in the respiratory quotient following upon severe phys. exertion is believed to be due to the rapid diffusion into the blood of the lactic acid that is present in large quantity in the muscle throughout the exertion.

L. W. RIGGS

Cholesterol and hemolysis. A. H. ROFFO. *Compt. rend.* 180, 1529-30(1925).—The cholesterol and total lipid content of the serum of rats, ranging from 2 to 5 months in age, showed a general increase in both factors with the age of the animal. Hemolysis depends on 2 factors, viz., the cholesterol content of the serum and the variable resistance of the erythrocytes; the latter factor in turn depends on the content of non-volatile fatty acids in the serum.

L. W. RIGGS

The female sex hormone and the gestational gland. R. T. FRANK AND R. L. GUSTAVSON. *J. Am. Med. Assoc.* 84, 1715-9(1925).—The physiol. factors are discussed by F. and the chem. factors by G. Conclusions: The sex hormone is a sp. substance elaborated by the gestational gland. It is taken up by the lymph and blood stream and selectively utilized only by Muller's tract and the mammary glands. The chemistry of the sex hormone is not fully detd. but the results to date warrant the following conclusions: The active substance is a thermostable lipid of high mol. wt. It is sol. in all lipid solvents. It is sol. in water in the presence of certain extractives of the placenta. It contains C, H and O or possibly only C and H. It is not an ester or fatty acid. It does not give the cholesterol reactions, nor does it contain the C.O group.

L. W. RIGGS

The gastric secretion: Its bactericidal value to man. H. J. BARTLE AND M. J. HARKINS. *Am. J. Med. Sci.* 169, 373-88(1925).—Detns of the bactericidal action of gastric juices in relation to their acidity showed that 21 of 26 specimens examd. were not sterile, while the degrees of acidity varied from no free HCl to an HCl value of 100°. With juices below a free HCl value of 10° there was practically no germicidal activity. Gastric juices with a free HCl of 10° to 20° were more germicidal for *Strep. viridans* and *B. coli communis* than for the *Staphylococcus aureus*. With free HCl values of from 20° to 100° the germicidal value was well marked. Gastric juice with free HCl between 0° and 90° had, as a rule, no effect upon *B. acidophilus*, and where a germicidal action was apparent a prolonged contact was required.

G. H. S.

Effects of external heat upon the human body. RALPH PEMBERTON. *Am. J. Med. Sci.* 169, 485-9(1925).—The therapeutic application of external heat causes a

heightened blood flow, an increased metabolism and elimination of acids, chiefly  $\text{CO}_2$  which escapes through the lungs, urine, and sweat. This leaves an excess of alkali in the blood, changing its reaction. In the compensatory effort an excess of alkali is eliminated through the sweat and urine. G. H. S.

Studies in gastric analysis (double simultaneous fractional analysis). R. T. ELLISON. *Am J Med Sci* 169, 550-63(1925).—Simultaneous fractional gastric analysis from 2 points in the stomach definitely fixed 10 cm. apart give curves entirely similar in general characteristics except where influenced by biliary regurgitation. The acid values from the antrum are always higher than those from the fundus, except where the former are influenced by biliary regurgitation. The phys. properties of the 2 specimens differ, because of greater comminution of the test substance by the peristaltic activity of the antrum. The antrum, close to the pylorus, is the best place to study gastric function. Biliary regurgitation does not pass beyond the antrum and is not primarily a mechanism to neutralize a high gastric acidity. G. H. S.

Studies in calcium and blood coagulation (with special reference to the use of salted plasma as a method of estimating clotting time). C. H. SMITH. *Am J Med Sci* 169, 572-83(1925).—The blood is salted with hypertonic  $\text{NaCl}$ , and after diln. of the salted plasma with distd. water, as well as with 2 concns. of  $\text{CaCl}_2$ , the coagulation time is detd. During clotting the Ca principally involved is its ionizable and available form. The hypertonic  $\text{NaCl}$  used probably affects all elements involved in coagulation, and with Ca it causes an inactivation. With increasing concns. of  $\text{CaCl}_2$  in the diln. of salted plasma a gradual retardation of clotting time is observed. As the period between salting and the subsequent centrifugation is increased the clotting time of the salted plasma after diln. is shortened. In jaundice the clotting time may be normal; if delayed it does not parallel the intensity or duration of the condition. Consideration of the clotting time in nephritis necessitates a differentiation between available and non-available or protein bound Ca. G. H. S.

Experimental studies on the entrance of bile into the duodenum. A. WINKELSTEIN AND P. W. ASCHNER. *Am J Med Sci* 169, 679-80(1925).—There is no evidence of spontaneous contractions of the gall bladder in the dog, either under anesthesia or when fully recovered. The gall bladder may be emptied by manual expression after the sphincter of Oddi is relaxed, and also by the increase in intra-abdominal pressure at the end of inspiration. In the exptl. animal under anesthesia, direct or reflex stimulation of the gall bladder, whether by faradization, drugs, hormones, chemicals or mech. means, does not result in contraction or emptying. Animals recovered from the operative procedure show a passage of bile into the duodenum following the instillation of 25%  $\text{MgSO}_4$  or the passage of gastric chyme (but not after normal saline) into the duodenum. Probably the effects observed with these substances are referable to their effect in relaxing the sphincter of Oddi so that the bile is expressed by the intra-abdominal pressure at the end of each inspiration. G. H. S.

Influence of the gall bladder on intestinal motility. B. M. BERNSTEIN. *Am. J. Med Sci* 169, 838-42(1925).—The gall bladder has a definite secretion of hormonal type—an activator—which has a regulatory effect upon intestinal motility, and its absence causes an imbalance in the normal correlated action of the circular and longitudinal muscle fibers. G. H. S.

Experimental studies on the color of the bile from the gall bladder and liver. A. WINKELSTEIN AND P. W. ASCHNER. *Am J Med Sci* 169, 842-50(1925).—Bile in the common duct of fasting dogs was tarry in consistency and dark greenish brown in color, when the gall bladder was *in situ*. When obtained from the hepatic duct it was a bright yellow whether the dog was feeding or fasting (occasionally a slightly darker color shortly after operation). After cholecystectomy the bile from the common duct was light yellow in color and thin in consistency whether the dog was feeding or fasting. The instillation of 25%  $\text{MgSO}_4$  into the duodenum did not result in any change in color of the bile from the common duct, either before or after cholecystectomy. G. H. S.

Isoelectric point of the muscle membrane and its functional significance. F. HAFNER. *Arch exptl Path Pharmacol* 103, 307-18(1925).—With the use of frog muscle, a study was made of the effect of  $\text{pH}$  upon the relationship between membrane potential, colloid charge and contraction. The normal negative potential of the muscle membrane passes from between 50 and 47 (in an electrolyte-poor medium) through a neutral point, to a positive charge at a higher acidity. The limiting surfaces, muscle cell/medium, have their isoelec. point here.  $\text{NaCl}$  shifts this toward higher acidity. The observation of an inversion of Beutner's concn. effect and of the K current depends upon these relationships. The isoelec. point of the muscle colloid is identical with that

of the membrane. This argues for the concept of the membrane potential as a Donnan potential. Acid contraction of muscle is maximal with approximation to the isoelec. point, and is thus associated with discharge of the colloid. G. H. S.

Origin of "dynamic protein hyperthermia." WALTHER SCHMITT. *Arch. expll. Path. Pharmacol.* 106, 89-101 (1925).—A protein hyperthermia occurs in those normally eating protein; the condition is characterized by a quick elevation of temp., acceleration in pulse rate, stimulation of respiration, sensations of pressure in the head, flushing, sweating, and an increase in the insensible perspiration. With the administration of the same no. of calories of sugar the values remained at approx. normal levels. G. H. S.

Chlorine exchange between the red blood cell and the surrounding fluid. III. Effect of the hydrogen-ion concentration upon the exchange. W. BURGER. *Arch. expll. Path. Pharmacol.* 106, 102-7 (1925).—When held in an acid phosphate soln for 30 min. less Cl passes into the fluid than when held in an alk. phosphate. After 4 hrs., however, the results are in both cases essentially the same, indicating that in 1 case a simple inhibition of diffusion is operative. Structural damage to the erythrocytes does not change the nature of the results, and the addn. of peptone (0.01 to 1%) to isotonic  $\text{Na}_2\text{SO}_4$  solns. has no demonstrable effect. The Cl exchange occurring within 30 min. was detd. in isotonic solns. of Na, K and Ca nitrates, as well as in Na and K sulfates. Considerably more Cl appears in nitrates than in sulfates, but the nature of the cations appeared to be without effect. An equil. between the cell and the fluid was reached much more quickly in nitrates than in sulfate or in phosphate solns. G. H. S.

Effect of the exclusion of the liver upon the intermediary protein metabolism of geese. M. FRHR V. FALKENHAUSEN AND P. SWON. *Arch. expll. Path. Pharmacol.* 106, 126-34 (1925).—The liver does not play a role in all phases of the intermediary metabolism of proteins. In the deamination of amino acids it is not concerned. With the injection of large amts. of amino acids into the circulation  $\text{NH}_3$  production takes place at exactly the same rate whether the liver is excluded or not. On the contrary, the synthesis of urea from  $\text{NH}_3$  appears to be an exclusive function of the liver. No data are at hand on the question of a possible extrahepatic formation of uric acid. G. H. S.

Function of the kidney nerves. PH. ELLINGER AND A. HIRT. *Arch. expll. Path. Pharmacol.* 106, 135-208 (1925).—The innervation mechanism of the kidney is definitely more complicated than has been assumed; there are nerves which regulate the amt. of urine, and others which modify urinary compn. without altering the amt. The superior renal nerve controls water and electrolyte elimination without modifying the other components, presumably through changes in the blood flow through the kidney. The inferior renal nerve inhibits  $\text{NH}_3$  formation and the excretion of total acids and of phosphates, and to a slight degree stimulates the output of total N. The great splanchnic functions as an antagonist to the inferior renal, favoring  $\text{NH}_3$  formation and the excretion of total acids and phosphates, and inhibiting, in a considerable measure, the excretion of total N. The vagus has an effect upon water elimination, although the mechanism of its action is not entirely clear. It also inhibits the output of total N. G. H. S.

Formation of urine in the frog kidney. III. Excretion of acid dyestuffs by the surviving frog kidney. HANS SCHULTEN. *Arch. ges. Physiol.* (Pflüger's) 208, 1-15 (1925).—The surviving frog kidney concentrates highly dispersed dyestuffs, dilutes medium ones, and is impermeable to colloidal dyestuffs. During narcosis and KCN intoxication the frog kidney is impermeable to dyestuffs, and when in these conditions, as well as when the H-ion concn. is increased, the amt. of dyestuffs to be found in the urine is diminished. In narcosis and in KCN intoxication the kidney is also impermeable to proteins, and the administration of protein causes a marked reduction in secretion. When the kidney is perfused with protein-contg. solns. of dyes the concn. of dye to appear in the urine is much lower than when the perfusion fluid is a dye-Ringer soln., a condition probably due to the fact that there is an adsorptive union between dyestuff and protein. Vital staining of the surviving tissue does not usually take place. G. H. S.

Significance of the electrokinetic potential for the study of biological surfaces. HANS NETTER. *Arch. ges. Physiol.* (Pflüger's) 208, 16-40 (1925).—The cataphoretic potential of red blood cells can, in general, be measured in terms of the relationship of the electrokinetic to the thermodynamic potential. It is found to be dependent upon the dissociation of the proteins present in the surface layer and upon the salt content of the soln. Washed and unwashed horse and beef red blood cells have approx. the same potential in serum, normosal and 0.95% NaCl. For unwashed horse and beef cells the isoelec. point is different in half-isotonic phosphate, NaCl and  $\text{CaCl}_2$  solns.; for

horse erythrocytes, 4.2, for beef, 3.8. For unwashed cells in M/40 to M/100 acetate the isoelec. point is the same for both (4.7), and in M/2000 it is between 5.2 and 5.4. The acetate concn. modifies, as this shows, the location of the isoelec. point. With washed horse cells in all solns. tested the isoelec. point is the same as that for unwashed cells, but with washed beef cells in M/40 acetate the value is 4.3, in M/2000 it is 4.7. Conclusion: The beef cells are enclosed in an albumin layer, the horse cells in a globulin layer. The common isoelec. point of unwashed cells of both types in acetate solns. is explained by the assumption that when transferred to the salt-poor acetate solns. the residual serum globulin present is pptd. on their surface, so that both types of cell behave as though they were enclosed in globulin with an isoelec. point of 5.4. Considering the relation of potential to stability it is shown that the height of the critical potential, that is, the highest potential at which agglutination still takes place, differs with hydrophilic colloids according to the magnitude of the cohesive force and the solvent affinity, and that both of these are dependent upon the material of the surface and the salt content. Consequently the critical potential of cells is influenced by the amt. and type of salt present. G. H. S.

Humoral transfer of skeletal muscle stimulation from one frog to the intestine of a second frog. R. BRINKMAN AND M. RUTTER. *Arch. ges. Physiol.* (Pflüger's) 208, 58-62(1925).—A positive result, as indicated by the title. G. H. S.

Urine formation in the frog kidney. V. The osmotic activity of the isolated frog kidney. W. DEUTSCH. *Arch. ges. Physiol.* (Pflüger's) 208, 177-83(1925).—By applying micro-methods to detn. of osmotic activity with the frog kidney it is found that the concn. of the urine follows changes in the concn. of the perfusion fluid when the latter is rendered either hypo- or hypertonic. But in both instances the kidney effects a further diln. As regards reversible and irreversible effects the kidney is sensitive to both hypo- and hypertonic fluids. The threshold, up to which a reversible perfusion is possible, is, for hypotonic solns., 6/10 Ringer; with hypertonic solns. the effects of a 10/8 Ringer are not completely reversible. A perfusion fluid in which half of the Cl is replaced by SO<sub>4</sub> causes an increased osmotic value. Perfusion with a fluid in which SCN is substituted for 0.4 of the Cl shows that the SCN passes through the kidney almost unaltered, while the Cl is dild. as in usual perfusion, indicating that SCN increases the osmotic concn. of the urine. G. H. S.

Physiology of the thyroid and of the parathyroids. II. Significance of the parathyroids to the body and the possibility of compensating for them. F. BLUM. *Arch. ges. Physiol.* (Pflüger's) 208, 318-33(1925).—The parathyroids pour out an internal secretion, a hormonogen, which is activated outside of the gland into a true hormone and as such circulates in the blood stream in excess. During lactation a certain amt. of the excess appears in the milk, conferring upon the milk the properties characterizing the parathyroid hormone. Through this hormone the parathyroids exert a profound influence upon many organs which is essentially a protective action against a continually threatening autointoxication. This protection extends to the central nervous system, the tissues leading to bone and tooth formation, to the lens and iris of the eye, to the kidneys, liver and hematopoietic app., to the thyroid, and probably to other organs and structures. These are all impaired if the parathyroids are eliminated beyond compensation; but if a fragment of parathyroid remains, or the diet (milk, blood) contains a minute quantity of the protective hormone the consequences of parathyroid deprivation are somewhat neutralized. In the adult animal the deficiency in parathyroid tissue is compensated for by the mobilization of latent principles. In youth such a mechanism is lacking; hence during this period a functional reduction in parathyroid activity is particularly significant. During the nursing period the mother contributes the essential factors through the milk. G. H. S.

Vital staining of the central nervous system. JULIUS SCHUSTER. *Arch. Psychiat. u. Nervenheilk.* 73, 657-719(1925).—The chem. and phys. properties of dyestuffs are considered in relation to their theoretical and practical utility in staining different elements of the central nervous system. G. H. S.

Relation of vital capacity to certain psychological characters. K. J. HOLZINGER. *Biometrika* 16, 139-56(1925).—There is a significant and essentially positive correlation of 0.12 to 0.16 between vital capacity and the 3 psychological factors, reaction time to sight, reaction time to sound, and acuity of sight. No correlation exists between vital capacity and acuity of hearing. Probably the correlation found is partly due to the influence of intermediate factors such as nervous and mental fitness which are in turn related to vital capacity. G. H. S.

Agglutination of human erythrocytes. JOHANNES BROBERSEN. *Z. Anat. Entwicklungsge.* 76, 91-103(1925).—Human erythrocytes are agglutinated by very diverse

substances—an acid (HCl), an alkali (NaOH), a carbohydrate (glucose) and a protein (gelatin). Erythrocytes agglutinate with each other, but not with leucocytes or platelets, or with frog erythrocytes. For agglutination a definite osmotic pressure of the agglutinating fluid is essential; with too high or too low a pressure the phenomenon does not occur. Only within limits is it true that the more concd. the agglutinator the stronger is the agglutination. Substances which have a tendency to make the cells round exert a deagglutinating effect. G. H. S.

## G—PATHOLOGY

H. GIDEON WELLS

**Physicochemical constants of serums. I. Variations of electrical conductivity with dilution.** P. LASSEUR, F. GIRARDET AND H. VERMELIN. *Bull. soc. chim. basl.* 7, 401-18 (1925).—Cond. measurements have been made with the serums of pregnant woman and of tuberculous and other patients, and with cerebrospinal fluid. The cond. of serums from normal and pathological individuals is approx. const., variations scarcely exceeding the limit of error and being of no diagnostic value. In pregnancy K varies from 109 to 126  $\times 10^{-4}$ , in tuberculosis 111 to 125  $\times 10^{-4}$ , and in healthy subjects and in various infections from 109 to 124  $\times 10^{-4}$ . The extremes noted for cerebrospinal fluid were 126 to 137  $\times 10^{-4}$ . Dilm. of cerebrospinal fluid leads to no differentiation. Serums with the same cond. give on dila. different values definitely greater than the limit of error. This effect is best shown at 1:1000. A. T. CAMERON

**The Abderhalden reaction.** EMIL ABDERHALDEN. *Fermentforschung* 8, 245-63 (1925); cf. C. A. 18, 3421.—A discussion of the reaction and its limitations and possibilities. Some minor changes in technic are proposed, such as the removal of proteins by heating the serum with  $\text{KH}_2\text{PO}_4$  directly in the centrifuge tube. A negative reaction is occasionally obtained with plasma while the corresponding serum gives a positive reaction. This may possibly be accounted for by a disintegration of blood platelets and leucocytes in the prepn. of the serum, and in that case the plasma would be more suitable for diagnostic work. Besides the use of the refractometer, the interferometer, the polariscope, the dialyzing app. and the detn. of sp. gr., the detn. of total and amino N in the dialyzate or in the protein-free fluid is recommended. A. W. DOX

**Experiences in the field of psychiatry and neurology with the micro-Abderhalden reaction.** PAUL BÜCHLER. *Fermentforschung* 8, 264-78 (1925).—In testing the sera of some 500 patients it was found that endogenous psychoses cannot be differentiated serologically. The blood of schizophrenics frequently shows protective enzymes. In psychoses the proteolytic enzymes observed are often due to disturbances in metabolism. With diseases involving internal secretion the micro-Abderhalden reaction gives results corresponding to the clinical phenomena; hence there is no justification for rejecting the assumption of dysglandular processes. Dysglandular, toxic and metabolic processes may play a significant part in the etiology of psychoses. A. W. DOX

**The presence of peptidase in experimental animals and in man, particularly in epileptics.** H. PREIFFER, F. STANDENATH AND R. WEBER. *Klin. Wochschr.* 4, 1122-3 (1925).—Normal serum contains a peptidase that hydrolyzes glycyltryptophan. Its concn. may vary from 30 to 75 units in different individuals but is fairly const. for a given individual. It is present in large quantities in normal feces. Adult urine may or may not (normally) contain this enzyme. It is present in quantity in the urine of young infants. The enzyme is probably derived from the intestinal contents. While free from attacks, epileptics are normal with respect to peptidase. Just preceding the attack the concn. of this enzyme is decreased in the urine and increased in the serum. After the attack the urinary output is markedly increased. During the attack (1 case) the concn. of the enzyme is decreased in both serum and urine. This suggests a retention in the tissues. MILTON HANKE

**Exercise and blood circulation.** HANS EFFINGER, FRANZ KISCH AND HEINRICH SCHWARTZ. *Klin. Wochschr.* 4, 1101-5 (1925).—Cardiac decompensation is characterized by an abnormally large vol. per minute output of the heart after exercising, a poor utilization of oxyhemoglobin, and a protracted increased utilization of oxyhemoglobin after the person has stopped exercising; this is due to an increased oxidation of the lactic acid produced in the muscle concomitant with the exercise. MILTON HANKE

**The two-phase action of hormones.** KURT KARGER. *Klin. Wochschr.* 4, 1165-6 (1925).—The intravenous injection of 100 mg.  $\text{CaCl}_2$  or  $\text{MgCl}_2$  raises the blood sugar value from about 0.1% to 0.14-0.18%. Max. values are obtained within 15-30 min., but the blood sugar remains high for 2 hrs. K. does not agree with Zondek and Ucko (cf. C. A. 19, 1868) that the action of insulin is two phase and that electrolytes enhance

the blood-sugar-elevating phase. He attributes the blood sugar elevation entirely to the electrolytes. MILTON HANKE

The dependence of the intraocular pressure upon the reaction of the blood. A. MEESMANN *Klin. Wochschr.* 4, 1214-5 (1925).—At a normal intraocular pressure the  $p_H$  of the blood ranges from 7.31 to 7.33. During pregnancy (low intraocular pressure) the  $p_H$  of the blood is 7.23-7.27. In chronic glaucoma (high intraocular pressure) the blood  $p_H$  ranges from 7.35 to 7.40. Glaucoma is occasioned by a swelling of the colloids in the eye due to increased alkalinescence. MILTON HANKE

The gold sol reaction in the cerebrospinal fluid. H. A. KAEBS *Klin. Wochschr.* 4, 1309-12 (1925).—Gold sols are negative colloids and can be flocculated only by positive colloids. Proteins are positive colloids only when the acidity of their sols. exceeds the isoelec point. The isoelec points of hemoglobin, globulin and albumin are, resp.,  $p_H$  6.8, 5.4 and 4.7. Obviously, then, a gold sol of low acidity might ppt. hemoglobin but not globulin or albumin. At a higher acidity globulin would ppt. while albumin would not. The gold sol reaction in the cerebrospinal fluid is dependent upon the  $p_H$  of the gold soln.; hence the latter must be standardized either by the gas chain method or by actual biological tests. An inactive sol can always be made active by a proper adjustment of its  $p_H$ . Albumin and globulin are not antagonistic. The globulin merely ppts. at a higher  $p_H$  than does albumin. In an alk. soln. both albumin and globulin function as protective colloids because their particles carry a negative charge. MILTON HANKE

Excretion of calcium by normal and diseased kidneys. G. HERÁNYI AND ST. V. NOGRÁDI *Klin. Wochschr.* 4, 1308-9 (1925).—Disturbances in the excretion of Ca always parallel the disturbances in the excretion of Cl and urea. MILTON HANKE

The behavior of the protein of the urine in the functional test of the kidney of Volhard. F. LASCH *Wiener Arch. inn. Med.* 9, 437-46 (1925).—A study of the changes of protein concn. in the blood and urine in the Volhard test for kidney function indicates that the excretion of protein is an active secretory function of the cells of the convoluted tubules. Quant. changes during the Volhard test indicate a good function and constancy of elimination; a destruction of the convoluted tubules. HARRIET F. HOLMES

Iodine hyperthyroidism and arrhythmia perpetua. O. ROTH *Wiener Arch. inn. Med.* 9, 475-98 (1925).—Auricular fibrillation was noted in 11 goiter patients with symptoms of I hypothyroidism. As it disappeared in one patient after thyroidectomy and in 2 patients after the hyperthyroid symptoms disappeared it may be considered as of thyrotoxic origin. I therapy in arteriosclerosis and syphilis may give rise to an auricular fibrillation. HARRIET F. HOLMES

Quinine-fast lipase in the serum of malaria patients. I. N. DIMITRIJEVIĆ *Wiener Arch. inn. Med.* 9, 499-502 (1925).—In the majority of cases of tertian malaria a quinine-fast lipase was found in the blood serum. The quinine-fast lipase occurs about as frequently as urobilinogen in the urine, though no direct relation could be established. It is probable that in malaria the liver is the source of the quinine-fast lipase. No atoxyl-fast lipase was found in the blood serum. HARRIET F. HOLMES

A rapid single test of kidney function with sodium iodide and thiosulfate. W. NITRI *Wiener Arch. inn. Med.* 9, 511-40 (1925); cf. C. A. 18, 3427.—A combined test of kidney function is described, with a single intravenous injection of 1 g. NaI and 1 g.  $Na_2S_2O_4$  in 10 cc.  $H_2O$  and examn. of the urine after 2 and 3 hrs. for the amts. of these substances eliminated. It was also found that most urines after being decolorized by charcoal bind a slight amt. of I, and that the urines of 2 diabetic patients bind a much greater quantity. HARRIET F. HOLMES

Study of the chemistry of pathological organs and the relations between the organs and fluids of the body. W. BERGER AND L. BLEYER. *Z. ges. expit. Med.* 45, 385-417 (1925).—In protein immunization and  $HgCl_2$  poisoning, changes in protein content run somewhat parallel. There is usually a relative and abs. decrease in sol. protein in muscles, liver and kidneys, a decrease in the total protein in muscles and kidney but not in the liver, an increase in residual N in the kidney, and a relative increase in albumin and globulin of the organs, due to an abs. decrease in sol. protein. No definite relation could be made out between the disappearance of sol. proteins, albumin or globulin in the different organs and the increased circulation of protein, albumin or globulin, in the serum. HARRIET F. HOLMES

The acid-combining power of the blood serum of healthy and diseased children. A. BOZÁNYI AND J. CASPÓ. *Biochem. Z.* 153, 185-90 (1924).—Blood (3 cc.) was taken from infants, allowed to stand until it began to retract, centrifuged and 1 cc. of serum obtained. This was treated with 0.02N HCl, and pptd. with  $K_2HgI_4$ , which pptd. protein as the HCl salt. After the ppt. was removed, the filtrate was titrated with NaOH

and the amt of bound HCl thus estd. The ratio (bound HCl/% protein present)  $\times 100$  = a quotient used for numerical comparison of different bloods. In normal infants, this quotient dropped from 92.4 at 2 months to 88.0 at 7 months and varied around 84-8 up to 14 yrs. In pulmonary tuberculosis it was 74.6-79.5, in scarlatina, 82-100, and was more nearly normal in many other diseases. The quotient may be raised either by increase of alkali in the blood, or by a change of globulin to albumin. W. D. LANGLEY

The factors in the dehydration following pyloric obstruction. J. L. GAMBLE AND S. G. ROSS. *J. Clin. Invest.* 1, 403-23 (1925).—The study of the acid-base equivalence of the blood showed that loss of chloride ions, by vomiting, in itself could not cause a fall in the total ionic concn. of the plasma because the bicarbonate ion is automatically adjustable. However, a simultaneous loss of Na ions accounts for the total fall in ionic concn. and leads to the removal of an equivalence of bicarbonate ions. The compensating effect of bicarbonate ions is further limited by increase in concn. of protein and possibly of org acids. Thus the alkalosis present in pyloric obstructions is actually far below what it might be. The loss of Na ions is the chief factor in dehydration since the vol of body water is dependent on the total electrolytes dissolved in the body. Dehydration can be repaired only by introduction of Na ions (as NaCl) and water, not by water alone (as in glucose soln) nor chloride ion alone (as in  $\text{NH}_4\text{Cl}$ ). After administration of NaCl soln the surplus of Na ions over chloride ions is excreted as bicarbonate in a urine of relatively high  $\text{pH}$ , thereby saving chloride ions for the body fluids.

LOUIS LEITER

The plasma proteins in relation to blood hydration. II. J. P. PETERS, H. A. BULGER AND A. J. EISENMAN. *J. Clin. Invest.* 1, 451-72 (1925), cf *C. A.* 19, 2369.—The plasma proteins are normal in mild diabetics, reduced in severe cases with chronic malnutrition. In toxemic diabetics with dehydration the plasma proteins appear high, but return to lower figures with increase in plasma vol. Dehydration is associated with acidosis. True diabetic edema rarely occurs in the presence of acidosis, but alkalosis is not essential. A nutritional factor must be of some importance in diabetic edema. Low plasma proteins and edema in severe diabetes are probably not related as cause and effect.

LOUIS LEITER

The glycogen content of the heart, liver and muscles of normal and diabetic dogs. N. F. FISHER AND R. W. LACKEY. *Am. J. Physiol.* 72, 43-9 (1925).—In diabetic (pancreatized) dogs the heart contained more glycogen (0.79%) than that of normal dogs (0.44%), while the liver and muscle contained less. Levulose was no better utilized for glycogen storage than was dextrose in the diabetic. When diabetic dogs are given insulin the glycogen content of the tissues approaches normal values. Normal dogs receiving excessive amts of insulin have a markedly decreased supply of glycogen.

J. F. LYMAN

The effect of thyroid therapy on the neuromuscular activity of cretinous sheep. H. S. LIDDELL AND S. STIMPSON. *Am. J. Physiol.* 72, 63-8 (1925).—The injection of thyroxin relieved symptoms of muscular weakness in thyroidectomized sheep. After thyroxin treatment there was a latent period of 3 to 5 days while thyroid ext. gave the same effect without a latent period. NaI was without effect.

J. F. LYMAN

Activity of human goiter tissue in tadpole experiments. C. WEGELIN AND J. ABELIN. *Arch. expil. Path. Pharm.* 105, 137-63 (1925).—The course of metamorphosis in tadpoles fed upon goiter tissue differs from the normal development as well as from the changes taking place in thyroid feeding. Loss in flesh, so characteristic a symptom of thyroid feeding, does not occur. The effects undoubtedly depend upon peculiar chem. structures, for with given tissues the effects cannot be referred to any other factor. Congenital glands, in the majority of cases, are without effect, a fact which correlates well with their deficiency or lack of colloid and their lack of I. Diffuse parenchymatous glands from children are relatively inactive while a similar tissue from adults gives typical effects. Diffuse colloid glands usually give strong and typical effects. Nodular glands are more frequently inert than are diffuse. Parenchymatous glands are always weak, often inert. In malignancy the results are always negative. In general, diffuse glands contain biol. active substances comparable in effect to those found in normal thyroid. Nodular glands are always less active. In both forms those rich in colloid are more active than are the parenchymatous tissues, although a strict parallelism between colloid content and biol. activity cannot be demonstrated.

G. H. S.

Blood-sugar studies. I. Rapid alteration on the blood-sugar level of rabbits as a result of intravenous injections of killed bacteria of various types. I. T. ZECKWER AND HELEN GOODELL. *J. Expil. Med.* 42, 43-56 (1925).—A rapid rise in the blood-sugar level of rabbits was produced by intravenous injections of killed *Bacillus proteus*, *B. coli* and *B. paratyphosus* B, which returned to nearly the previous level in a few hours.

time. A less pronounced rise in blood sugar was produced by killed *B. paratyphosus* A and *B. enteritidis* II. Blood sugar changes in fatal bacterial anaphylaxis in the rabbit. *Ibid* 57-67.—During bacterial anaphylaxis there is a gradual rise in the blood-sugar level, which attains an extremely high value at the time of death. The curve of blood sugar is quite similar whether anaphylaxis is induced by organisms which affect the blood sugar in the unsensitized animal or by organisms which have no such effect. No instances occurred in which there was not a marked hyperglucemia in anaphylaxis.

C. J. West

Surface tension of serum. XIV. The change in surface tension occurring as a result of immunization. P. LeCOMTE DU NOUY AND LILLIAN E. BAKER. *J. Exptl. Med.* 42, 9-15(1925), cf. *C. A.* 19, 2374.—The sera of rabbits, taken before injection and on the 13th day after immunization, were analyzed for the % of globulin and albumin,  $\text{Na}_2\text{SO}_4$  being used for the pptn of the globulin, and for N. No const. change of any magnitude occurred as the result of immunization. The magnitude of the time drop of all the sera on the 13th day showed the usual increase as the result of immunization. This increase cannot, therefore, be traced to an altered albumin-globulin ratio. Sera treated with antigen *in vitro* and incubated for 13 days at  $37.5^\circ$  showed no increase in the magnitude of the time drop. This increase must be due to an indirect action brought about through interaction with the tissue of the living animal.

C. J. W.

Relation of hyperglucemia to the relative blood volume, chlorine concentration and chlorine distribution in the blood of dogs. LEE FOSHAY. *J. Exptl. Med.* 42, 89-98 (1925).—In normal dogs exptl. hyperglucemia causes a prompt dila. of the circulating blood, evidenced in the increase in the relative vol. of serum and the reduction of the erythrocyte counts. If the hyperglucemia is large, the viscosity of the blood is visibly diminished. As the hyperglucemia increases there occurs a reduction of the serum Cl concn. and an increase in the concn. of corpuscular Cl. Reduction of an artificial hyperglucemia restores the relative blood vols. to their normal status. The erythrocyte count rises to the normal and the corpuscular Cl concn. is diminished. If the reduction is a large one, the viscosity of the blood is visibly increased. The same types of cond.-chloride discrepancy that occur in human blood are found in the blood of dogs. In addn., a 3rd type is described. Hyperglucemia does not cause the same changes in the vol. of the av. erythrocytes of the dog as it does with human erythrocytes.

C. J. W.

Urobilin physiology and pathology. IV. Urobilin and the damaged liver. ROBERT ELMAN AND PHILIP D. McMASTER. *J. Exptl. Med.* 42, 99-122(1925); cf. *C. A.* 19, 2233.—Evidence is presented which supports the view that in the uninfected animal the intestinal tract is the only place of origin of urobilin, not merely under normal circumstances but when there is biliary obstruction. Animals rendered free of urobilin by collection of all the bile from the intubated common duct remain urobilin-free even after severe hepatic injury. Urobilinuria was never found after liver damage except when bile pigment was present in the intestine. It appeared during the 1st days after ligation of the common duct, but disappeared as the stools became acholic. When this had happened a small quantity of urobilin-free bile, given by mouth, pptd. a prompt urobilinuria. After obstruction of the duct from  $1/2$  of the liver, mild urobilinuria was found, but no bilirubinuria. In animals intubated for the collection of a part of the bile only, while the rest flowed to the duodenum through the ordinary channels, liver injury caused urobilinuria, unless indeed it was so severe as to lead to bile suppression, when almost at once the urobilinuria ceased, though the organism became jaundiced. This proves that urobilinuria is an expression of the inability of the liver cells to remove from circulation the urobilin brought by the portal stream, with the result that the pigment passes on to kidney and urine. Urobilinuria occurs with far less degree of liver injury than does bilirubinuria.

C. J. West

MELANBY, EDWARD: Experimental Rickets. Effect of Cereals and Their Interaction with Other Factors of Diet and Environment in Producing Rickets. London: H. M. Stationery Office. 66 pp. 3s. 6d. net. Medical Research Council Special Rept. Series No. 93.

## H—PHARMACOLOGY

ALFRED N. RICHARDS

Influence of emetine on protoplasmic activity. A. BALDONI. *Biochem. terap. sper.* 10, 303(1923); *Arch. ital. biol.* 74, 74(1924).—Its toxicity is relatively slight on lower forms of life. In concns. of 1:1000 it depresses the oxidase activity of the potato. Concns. of 1:5000 immobilize paramecia in 3 hrs. and of 1:30000 in 6 hrs.

A. T. C.

Behavior of salicylic acid in the human organism. A. BALDONI. *Biochim.*

*terap. sper* 10, 271(1923); *Arch. ital. biol.* 74, 75(1924) —It is excreted unchanged.

A. T. CAMERON

Synthesis of salicyluric acid in some pathological conditions. A. BALDONI. *Biochim. terap. sper.* 10, 335(1923); *Arch. ital. biol.* 74, 75(1924).—Hepatic fusions prevent this synthesis in man; kidney lesions probably favor it.

A. T. CAMERON

Iron exchange with special regard to the reticulo-endothelial apparatus. P. OCCHIONI. *Minerva med.* 3, 145, 177(1923); *Arch. ital. biol.* 74, 80(1924).—A histochem. study.

A. T. CAMERON

Pharmacological and toxicological studies on the arsenobenzenes. A. PATTA. *Biochim. terap. sper.* 10(1923); *Arch. ital. biol.* 74, 80-1(1924).—Different substitution derivs. of dihydroxydiamminarsenobenzene, considered as corresponding to Ehrlich's "914"; each possesses a different degree of toxicity.

A. T. CAMERON

An efficient intestinal antiseptic. The perchlorides of mercury and iron in combination. T. S. WILSON. *Brit. Med. J.* 1924, 1, 270-1 —This should be given 15 min. before meals. Good results are claimed in cases of enteric fever, colitis and dysentery.

A. T. CAMERON

Special discussion on endocrine therapy. LANGDON BROWN, SWALE VINCENT, LESLIE PUGH, H. GARDINER-HILL, K. WALKER, H. C. MILLER, J. E. R. McDONAGH AND M. B. RAY. *Proc. Roy. Soc. Med.* 18, 25-48(1925) —A discussion chiefly dealing with the relationship between exptl. and clinical observations.

A. T. CAMERON

Mechanism of therapeutic action of suspensoids. J. LOISELEUR. *Bull. soc. chim. biol.* 6, 661-4(1924).—Colloidal and flocculated ovalbumin and serum have been subjected under the same conditions to the actions of colloidal Au, Bi, Rh and Ag. Hydrolysis of the colloidal soln. is impeded; that of the flocculate is increased. The results suggest that the therapeutic effects of suspensoids depend on an elective action on the flocculated material of the blood, while they have no action on the normal colloidal constituents.

A. T. CAMERON

A case of diabetic coma treated with dihydroxyacetone with recovery. I. M. RABINOWITCH. *Can. Med. Assoc. J.* 15, 520-2(1925); cf. C. A. 19, 1898 —Administration of repeated small doses of dihydroxyacetone without insulin was followed by definite decrease in blood glucose, increase in plasma  $\text{CO}_2$ , and gradual clinical improvement with disappearance of the coma at the end of 12 hrs.

A. T. CAMERON

A note on protagulin in hemorrhage after extraction. G. J. GOLDIE. *Proc. Roy. Soc. Med.* 18, Sect. Odontol., 19-26(1925).—Good results are claimed by use of this thrombin-contg. prepn.

A. T. CAMERON

Internal secretion (hormone) action of choline on the motor functions of the digestive tract. III. The formation of choline by degradation of compounds (phosphatides) of which it is a component. EMIL ABDEKHALDEN AND HANS PAFFRATH. *Fermentforschung* 8, 284-93(1925); cf. C. A. 19, 1910 —A quant. sepn. of free and combined choline may be effected by pptn. of the latter from its colloidal suspension by means of colloidal  $\text{Fe}(\text{OH})_3$ . The lecithin emulsion is made faintly alk. with 2-3 cc. of 0.1 N NaOH then 20 cc. of dialyzed  $\text{Fe}(\text{OH})_3$  soln. is added, the soln. filtered and the ppt. washed thoroughly with  $\text{H}_2\text{O}$ . The filtrate is slightly acidified with dil. HCl, evapd. to dryness, the residue extd. several times with hot EtOH and filtered. After evapn. of the solvent the choline is acylated and the acetylcholine detd. biologically (cf. C. A. 19, 1910). The ppt. contg. combined choline, with the filter, is refluxed 3-4 hrs. with 5%  $\text{H}_2\text{SO}_4$ , the latter removed by the exact equiv. of  $\text{Ba}(\text{OH})_2$ , the filtrate evapd. and the residue extd. with glacial AcOH. Detn. of acetylcholine is performed as before. Lecithin emulsion is not appreciably decompd. by intestinal bacteria until after several days and the fiberated choline is simultaneously broken down. The free choline disappeared completely in 18 hrs., whereas no decrease in combined choline was observed until after 120 hrs. although a distinct putrefaction odor was perceptible after 72 hrs. The surviving intestine of mammals under biol. conditions liberates in 8-10 hrs. 3-5 times the amt. of free choline originally present, while the amt. of combined choline decreases to  $1/3$ . The amt. of cleavage is dependent upon the condition of the intestinal cells. Chilling in a freezing mixt. does not impair the lecithin-splitting power of the cells. Intense freezing with  $\text{CO}_2$  snow, however, followed by thawing out of the tissue, diminishes the cleavage power, as does also treatment with distd.  $\text{H}_2\text{O}$  or 0.1 N KCN. The lecithin cleavage is probably an enzymic process. IV. Degradation of phosphatides by press juice from the small intestine. *Ibid.* 294-8. —In the press juice of hog intestine an enzyme was demonstrated repeatedly but not invariably which has the power of hydrolyzing egg and intestinal lecithin, so that the increase of free choline and the decrease of combined choline could be followed. The enzyme is inactivated by 2 hrs. heating at 55-60°. Since the free choline liberated by the surviving intestine

originates mainly from the phosphatides of the intestinal wall, and since the extent of the cleavage is influenced by stimulation of the Auerbach plexus, it must be assumed that the process is under nerve control. V. Synthesis of choline esters from choline and fatty acids by means of enzymes of the small intestine. *Ibid* 299-307.—The surviving small intestine of the hog and of the horse and the press juice from hog intestine contain an enzyme which hydrolyzes acetylcholine into its components. Inactivation of the enzyme results from 2 hrs' heating at 70-5° but not at 55-8°. In concd. (10-30%) choline-NaOAc solns the enzyme synthesizes acetylcholine to the extent of 0.2-0.8%. Diln then reverses the process. Synthesis is dependent on the reaction; in alk. soln it does not occur, but it reaches its max in the presence of strong AcOH. The significance of this observation is that inactive amts of choline may become strongly active by acetylation when necessary and the physiol action again diminished by reversal of the process. A. W. DOX

Activation of insulin with protein. FERDINAND BERTRAM *Klin. Wochschr.* 4, 1107-9(1925).—The action of insulin is intensified and more protracted when the insulin is mixed with protein (casein) before injection. Protein alone is without effect. When separately injected, the protein does not intensify the action of insulin. MILTON HANKE

Therapeutic investigation with irradiated milk in rickets. P. GYORGY. *Klin. Wochschr.* 4, 1118(1925).—Salad oil or milk, when exposed to ultra-violet light, acquires an odor and a taste resembling cod-liver oil. Irradiated milk, like cod-liver oil, is antirachitic. MILTON HANKE

Difference in action of various insulin preparations clinically and in animals. Standardization of insulin; an analysis of cases that are apparently refractory to insulin. RICHARD PRIESEL AND RICHARD WAGNER *Klin. Wochschr.* 4, 1157-9(1925).—Samples of insulin from different com. sources that are identical in activity as measured by animal expts may be very different clinically. A French prepn was entirely ineffective in 1 case in which smaller concns of a British prepn were very effective. In some other cases the 2 prepn were almost identically active. MILTON HANKE

Acid poisoning. L. HESS AND J. GOLDSTEIN. *Wiener Arch. inn. Med.* 9, 461-72(1925).—Rabbits injected with trypan blue were compared with rabbits injected with the vital stain and then given 0.25 N HCl by gastric tube. The acid treated rabbits showed foci of necrosis in the liver with loss of dye from the parenchyma cells and the Kupfer cells. This alteration of the liver cells may be an important factor in the pathology of acidosis. HARRY F. HOLMES

Physiological action of acetone bodies. M. I. LIPSCHITZ. *Z. ges. expil Med.* 45, 432-8(1925).—Acetone and the ethyl acetate have little effect on the circulation in small doses but in large doses lower blood pressure, the former with a slight increase in pulse rate and the latter with a decrease.  $\beta$ -Hydroxybutyric acid causes a marked rise of blood pressure with sometimes a marked decrease in pulse rate. Acetone when applied to isolated muscle and nerve decreases the irritability. HARRY F. HOLMES

The reactions of the pupil in the chloralosed animal. R. J. S. McDOWALL. *Quart. J. Expil Physiol.* 15, 177-80(1925).—The reactions of the pupils of chloralosed animals may be used as an index of sensation not only from areas supplied by the spinal nerve but also from those supplied by the autonomic nervous system. FRANCES KRAKOW

Review of the field of pharmacology. CARL BACHEM. *Zentr. inn.* 44, 725-40, 753-62(1923). *Med.* 45, 91-102, 425-39, 449-58, 769-84(1924). J. H. LEWIS

The sugar concentration in arterial and venous blood during insulin action. C. F. CORI AND G. T. CORI. *Am. J. Physiol.* 71, 688-707(1925).—Difference in dextrose content of arterial and venous blood before and after insulin administration indicates that insulin increases the rate at which dextrose disappears from the blood into the muscles. This is the case in the partially starved rabbit, the sugar-fed rabbit, in normal men and in diabetic patients. J. F. LYMAN

The insulin content of the pancreas and other tissues in animals poisoned with phlorhizin. G. T. CORI. *Am. J. Physiol.* 71, 708-13(1925).—No appreciable diminution of the insulin content of the organs of phlorhizinized animals could be detected. J. F. LYMAN

Phosphorus poisoning in a child from the ingestion of fireworks. H. L. DWYER AND F. C. HELWIG. *J. Am. Med. Assoc.* 84, 1254-6(1925).—A three year-old boy died 4 days after eating a kind of fireworks known as "spit devil" which contained yellow P. In expts with dogs receiving this poison, the most effective treatment was the administration of liquid petrolatum or lavage within 2 hrs after the lethal dose was taken. L. W. RIGGS

Antagonistic action of posterior pituitary extract and insulin. R. C. MOENIG

AND HARRIET B. AINSLEE. *J. Am. Med. Assoc.* 84, 1398-400(1925).—Expts. with rabbits showed that posterior pituitary ext. injected into normal animals produces, as a rule, a slight rise in blood sugar. The same ext. when injected simultaneously with insulin prevents the fall produced by the latter. The ext. injected during insulin hypoglycemic convulsions produces a rapid rise in blood sugar, with subsequent recovery of the rabbits. The point of attack of the pituitary ext. seems to be in the periphery; viz., the skeletal muscle metabolism. L. W. RIGGS

Effect of radiations of cod-liver oil. Preliminary note. I. A. MANVILLE. *J. Am. Med. Assoc.* 84, 1401-2(1925).—Besides the action of cod-liver oil in curing or preventing rickets, there are 2 other specific actions: viz., (a) a stimulation of cell activity and a distinct inhibitory effect on bacterial growth, (b) when these active substances are in excess of the quantity producing stimulation, there is exerted a depressing action, the most striking manifestation of which is a lack of fertility. The sepn. of fat-sol. A into 2 sep. vitamins each with a specific action does not seem justified when the effects can be explained as being due to different concns. of the same principle. L. W. RIGGS

Localized gangrene following the hypodermic administration of calcium chloride. M. G. SEZLIG. *J. Am. Med. Assoc.* 84, 1413-4(1925).—CaCl<sub>2</sub> solns. of 2% and over show a marked tendency to cause necrosis when brought into contact with subcutaneous tissue. When solns. of such strength are used for intravenous administration, necrosis and gangrene constitute a real menace because of the danger of some of the soln. escaping into the perivenous tissues. The poisonous effect of CaCl<sub>2</sub> (cardiac depression) may be discounted in a large measure because the dosage commonly used is not large enough to cause toxic symptoms, particularly if the soln. is given slowly. A 1% soln. (50 cc.) administered slowly seems to avoid all undesirable effects. L. W. RIGGS

Toxicity of the castor bean. F. L. FOLLWEILER AND D. E. HALEY. *J. Am. Med. Assoc.* 84, 1418(1925).—Three cases of severe poisoning developed among workers in the Penn. State Coll. lab. during a research upon the castor bean, particularly upon the *Ricinus* lipase. The eyes, nose, throat and lungs showed an edema, accompanied by abdominal pains, vomiting, diarrhea and extreme prostration. Recovery gradually ensued when the workers remained away from the lab. The poisoning was so serious that the research was abandoned. L. W. RIGGS

Oxygen therapy in pneumonia. A. E. GUEDEL. *J. Am. Med. Assoc.* 84, 1490-1(1925).—The present unpopularity of O therapy in pneumonia is the result of faulty and skimping technic. With the first appearance of cyanosis of the finger nails O is administered and continued until the finger nails remain pink after the removal of the O. L. W. RIGGS

Effect of germanium dioxide on the rabbit. G. H. BAILEY, P. B. DAVIDSON AND C. H. BUNTING. *J. Am. Med. Assoc.* 84, 1722-4(1925).—Contrary to the results published by others, GeO<sub>2</sub> was not found to be a hematopoietic stimulus in the rabbit. Although the rabbit may survive a large dose of GeO<sub>2</sub> (more than 200 mg. intraperitoneally) yet in doses as small as 4 mg. the drug is toxic for the main parenchymatous organs, resulting either in the death of cells, or in an eventual atrophy following a state of hydropic degeneration with increased autolysis. L. W. RIGGS

Heinrich Dreser. H. H. MEYER. *Arch. exptl. Path. Pharmacol.* 106, No 3-4, i-vii(1925).—An appreciation of the contribution of Dreser to pharmacology, together with a bibliography of his publications. His death occurred on Dec. 21, at Zurich. G. H. S.

Pharmacology of the frog heart. HEDWIG LANGECKER. *Arch. exptl. Path. Pharmacol.* 106, 1-77(1925).—A type of toxic heart arrest occurs through stimulation of the vago-accelerans, under conditions recalling the results of Hering on the reactivation of the arrested mammalian heart by isolated accelerans stimulation, as well as those of Löwit on the restored action of hearts arrested by muscarine through vagal stimulation. The phenomenon of "vagal paralysis" by adrenaline is only to be explained as due to the predominance of toxic-stimulated accelerans. The so-called "sympathetic-frog" is perfectly susceptible to vagal stimulation. Vagus paralysis during the bradycardia stage of muscarine poisoning is dependent upon increased irritability of the sympathetic caused by the muscarine. Physostigmine has an effect, hitherto entirely overlooked, on the sympathetic, increasing the irritability to a degree far in excess of the increase in vagus irritability. In frogs, just as in mammals, pilocarpine causes a true paralysis of the vagus. The nature of the effect of vagal stimulation in frogs subjected to chloral depends upon whether the vagus is hyperirritable or whether the irritability of the sympathetic predominates. All of the poisons studied which stimulate the parasympathetic increase the irritability of the accelerans. There are no poisons which stimulate the parasympathetic only; acetylcholine most nearly accomplishes this. Acetylcholine arrest

may be differentiated from that of muscarine. In view of the conclusion of Fredericq concerning the paralysis of the accelerans endings by caffeine, its antagonistic action in muscarine, pilocarpine and acetylcholine arrest is to be considered as a pure direct stimulation of the primary stimulus formation which is associated with the paralysis or the reduction in irritability of the sympathetic. There is a possibility that caffeine, and perhaps other substances also, may modify heart qualities at times through the endings of extracardiac heart nerves and at other times through a direct effect upon the substrate involved. Camphor may abolish pilocarpine or acetylcholine arrest, and, indeed, in the latter it is superior to adrenaline in the rapidity of its effect. G. H. S.

Blood of the bone marrow in dogs. II. Mechanism of the action of adrenaline upon the bone marrow. RUDOLF SCHÖEN. *Arch. expil. Path. Pharmacol.* 106, 78-88 (1925), cf. C. A. 19, 1602.—The observed effects of adrenaline upon the bone marrow are apparently due to a direct stimulation of the sympathetic end-app., which results in an outpouring of blood cells. Preliminary administration of ergotamine prevents this adrenaline effect. Pilocarpine is without effect upon bone marrow. The passage of blood through the bone marrow is markedly diminished by adrenaline. Increase in blood pressure or asphyxia does not cause an adrenaline effect on the marrow.

G. H. S.

Effect of Congo red upon intoxication by pancreatic autolyzates. H. PFEIFFER AND F. STÄNDENATH. *Arch. expil. Path. Pharmacol.* 106, 108-14 (1925).—Congo red injected into the peritoneal cavity or into the circulation exerts a striking protective action against subsequent intoxication by the intraperitoneal injection of pancreatic autolyzates. The protective action persists for a week. When injected subcutaneously it is without protective action, nor does it have any neutralizing action, in whatever way it may be introduced, when the autolyzate is given directly into the blood stream. Administered during an intoxication it is inert. No significant deposition of the colloid in the reticulo-endothelial app. occurs after intravenous injection even though the protective effect is clear-cut.

G. H. S.

Elimination of the stereoisomers of cocaine in the urine and its relation to their toxicity. ERICH GRÜHN. *Arch. expil. Path. Pharmacol.* 106, 115-25 (1925).—In comparison with other preps. *l*-cocaine is eliminated in the urine to by far the greatest degree. Even in doses 2 to 3 times as large *d*-cocaine and *d*-pseudococaine are eliminated in smaller amts. than is the *l*-form. This affords support for the assumption that the lower toxicity of the *d*-form depends upon its more rapid detoxication and its more complete destruction. No evidence is adduced here to show whether detoxication depends upon adsorption or destruction. Excretion rates and the toxicity of cocaine and *d*-pseudococaine are not parallel, for cats reacted strongly with convulsions to 38 to 46 mg. per kg. of *d*-pseudococaine while they manifested no symptoms at all to the same quantities of cocaine. Nevertheless, *d*-pseudococaine is excreted in smaller amts. It would appear that the relation between elimination rates and degrees of toxicity is more complex than would *a priori* appear, and that the spacial arrangements in the mole modify detoxication properties. With reference to the effect of repeated injections upon elimination it appears that during such a course of treatments toxicity is not diminished, whereas, at least in some cats, the degree of elimination (of *l*-cocaine in particular) is reduced. In other animals, receiving only the *l*- and *d*-normal cocaine, this diminution in excretion is not apparent.

G. H. S.

Pharmacological modifications in the dynamics of the frog heart. KARL JUNKMANN. *Arch. expil. Path. Pharmacol.* 105, 169-84 (1925).—The isometric tension max. of the frog heart increases with diminishing frequency, and is independent, within limits, of the reduced diastolic filling consequent upon the latter. The work of stretching developed by a normal frog heart is increased by adrenaline. With the fatigued heart it is difficult to increase the compression power. Here, not only adrenaline, but also caffeine, and to a certain extent physostigmine, are effective. It is of interest that digitalis and camphor are inert. Digitalis increases the isometric tension max. only when it has been reduced by injury of a definite type, as, after damage by quinine (camphor was not tested) and by Ca deficiency. It is not effective after injury by chloral hydrate. Caffeine, on the other hand, increases compression power when diminished by chloral. The increase in the power of the normal heart due to caffeine may be considered as purely a result of increased frequency. The same antagonistic effect with digitalis or caffeine on the one hand and different heart-paralyzing agents on the other indicates that it is a result of a positive inotropic action. But with digitalis this must be of a nature differing from that with caffeine. With camphor there is simply a negative inotropic effect. The described increase in the min.-vol. by camphor after intoxication

by chloral hydrate and alc. may be associated with the vagus-paralyzing action of the camphor. G. H. S.

Disturbances in the oxidative breaking down of carbohydrate caused by phlorhizin. So-called renal glucosuria. ALFRED GOTTSCHALK. *Arch. expil. Path. Pharmacol.* 106, 209-13(1925).—Phlorhizin, as has been shown to be the case with adrenaline, suppresses acetaldehyde formation by the surviving liver cells of warm-blooded animals. G. H. S.

Protective action exerted by some colloidal substances against intoxication by curare. J. R. PETROFF. *Arch. expil. Path. Pharmacol.* 106, 214-22(1925).—No material protection against curare intoxication is afforded by gum arabic, India ink, casein, ferrous oxidatum dialysatum, vesuvium, animal charcoal or collargol. Aniline blue (particularly) and azo blue weaken the effect of curare. The many substances tested may be divided into 3 groups: those which do not exert a sp. action against curare either when added to a curare soln. *in vitro* or when introduced into the body; those which diminish the effect of curare only when added to it *in vitro*; and those which reduce the action whether combined with the curare *in vitro* or introduced into the body. The majority of substances having a protective effect manifest the action both *in vitro* and *in vivo*. Exceptions are charcoal suspensions and colloidal Ag, which are effective *in vitro* only, a fact of some significance perhaps, since these substances (like ink, which is here inert) strongly stimulate the reticulo-endothelial app. This and the *in vitro* action exclude cellular function as being involved in the mechanism of the protective effects exerted by dyestuffs for curare. Quant. values obtained with Congo red indicate that even in equal quantities the weakening effect is observed, with a corresponding reduction in the action of the curare as the amt. of Congo red is increased. A complete protection is obtained when the amt. of the dye is 10 to 20 times that of the curare. The union of dyestuff with curare is relatively resistant to heat, and also resists standing for at least 24 hrs. G. H. S.

A reversed adrenaline effect on the intestine and uterus in the presence of copper salts. FUMIO HAZAMA. *Arch. expil. Path. Pharmacol.* 106, 223-32(1925).—Copper salts, as well as the salts of Fe, Pt and Ba, in extremely small quantities are able to reverse the action of adrenaline on smooth-muscle autonomic innervated organs, as is shown by reactions on the intestinal muscle of rats, rabbits and frogs, and on the uterine tissue of rats, cats and rabbits. A study of the action of adrenaline on the blood pressure of the intact animal after preliminary treatment with Cu salts led to no results with regard to a higher toxicity. On the isolated cold-blooded heart a corresponding effect of Cu salts was not obtained. The reversal of adrenaline action takes place quite without regard to whether the Cu and the adrenaline act upon the organ concerned independently or otherwise. The reversed action of adrenaline might be interpreted as a tendency to strengthened Cu action resulting from an increase in permeability due to adrenaline. One cannot view the increase in the tonus of the vagus caused by Cu as the sole cause of the adrenaline reversal, since, in the first place, amts. of Cu which are without demonstrable effect on the intestinal tonus reverse the reaction of adrenaline, and, in the second place, an increase in the tonus of the vagus by pilocarpine or choline does not reverse the effects of adrenaline. Whether the increased tonus and peristalsis induced by adrenaline after preliminary treatment with Cu represent a stimulation of the parasympathetic nerve endings must also remain undecided, although such a possibility receives some support from the fact that small doses of atropine exert an antagonistic influence. G. H. S.

Toxic properties of diethylphthalate. O. M. SMITH. *J. Am. Pharm. Assoc.* 13, 812(1924).—Doses up to 0.5% of body wt. to rats per ora caused pain, weakness and distress for 10-12 hrs.; after 24 hrs. the animals were normal. Pregnant rats were not prematurely delivered by 0.5% of body weight. Pulets were unable to walk after doses of 1.5% of body weight but were normal in 12 hrs. Large doses passed unchanged. Humans working in contact with the substance are not poisoned but solns. in EtOH are irritant to mucous membranes. L. E. WARREN

Hg derivatives of azo dyes (PROSKOURIAKOFF, RAISS) 10. Catalytic reduction of chaulmoogric and hydnoaropic acids (DEAN, *et al.*) 10. Leprosy. XXXVII. Fractionation of chaulmoogra oil (WRENSHALL, DEAN) 10.

KOPACZEWSKI, W.: Pharmacodynamie des colloides. Vol. 2. Proteinotherapie et transfusion du sang. Paris: G. Doin. 340 pp. Fr. 8. Cf. C. A. 18, 1715.

MÖLLGAARD, HOLGER: Chemotherapy of Tuberculosis. Copenhagen: Nyt Nordisk Forlag. 419 pp. R. M. 25.

## I—ZOOLOGY

R. A. GORTNER

The problem of the recent melanism of butterflies. VII. The independence of the blood melanogens with respect to the chlorophyll of the nutrient plant. K. HASSEBROEK *Fermentforschung* 8, 197-8(1925), cf. *C. A.* 18, 2923 —The blood from larvae of *Arctia caya* which had been fed green and white leaves, resp., of cabbage showed the same spontaneous darkening, indicative of the occurrence of melanogens formed independently of the presence of chlorophyll in the food. VIII. Further experiments on the melanizing action of atmospheric contaminations on the living pupa. The origin of municipal and industrial melanism through external influences. *Ibid.* 199-226 —A large no. of species gave unmistakable evidence of the darkening of color patterns when exposed in the pupal state to low concns. of  $\text{NH}_3$ , pyridine or  $\text{H}_2\text{S}$ . Other gases known to occur as atm. contaminations in industrial centers, e. g.,  $\text{CH}_4$  and illuminating gas, had less or no effect. In the vicinity of marshes melanism may occasionally be observed, especially where volatile putrefaction products of proteins are given off. Melanism has probably developed mostly during the past 80 years and may be attributed to atmospheric contaminations arising from modern industrial operations, since it is most noticeable in factory districts and in large cities. Inheritance and selection may also be factors in the progressive melanization of moths and butterflies. A. W. DOX

Studies on amphibian metamorphosis. II. JULIAN S. HUXLEY, *Proc. Roy. Soc. (London)* 98B, 113-46(1925); cf. *C. A.* 17, 2918 —Air breathing did not produce metamorphosis of *Axolotl*, but gave rise to disappearance of the fin, which fell to one side, then fused completely with the skin of the back. Tadpoles of the frog, *Rana temporaria*, were kept under narcosis for periods as long as 10 days by means of urethan; if they had previously been treated with thyroid, metamorphosis proceeded at the normal rate. Complete narcosis by urethan decreased the  $\text{O}_2$  consumption of both normal and thyroid-treated tadpoles by approx 40%. Metamorphosis of *Axolotl* was not produced by exposure to the most concd. tolerated soln. of I or by administration of I with the food, even in an atm. of  $\text{O}_2$ . However, pseudometamorphic changes occurred (protruding eyeballs, reduction of fins and gills), but not the irreversible moult. Exposure to an atm. of  $\text{O}_2$  caused poor growth and emaciation of tadpoles; pure  $\text{O}_2$  retarded the metamorphosis produced by  $\text{I}_2$  and thyroid, but normal metamorphosis occurred in a mixt. of air and  $\text{O}_2$  contg. 40%  $\text{O}_2$ . KCN retarded general growth and, to a greater degree, the metamorphosis produced by  $\text{I}_2$  and thyroid; susceptibility to its action increased with age. Alc. retarded this metamorphosis, in proportion to its concn. Administration of thyroid to adult male newts (*Triton cristatus*) during the breeding season did not produce any significant acceleration of the fin regression and loss of wt. In *Anura* the limbs are affected by a low, the tail by a high concn. of thyroid, while *Urodele* larval limbs are not affected. JOSEPH S. HERBURN

Glycogen differentiation in *Paramecium caudatum*. H. RAMELMAYER, *Arch. Protistenk.* 51, 184-8(1925) —In the first conjugation phase, glycogen is present in considerable amt. in the animals. The glycogen content is almost always equal in the 2 individuals. FRANCES KRASNOW

The relation of the stability of protoplasmic films in *Noctiluca* to the duration and intensity of an applied electric potential. E. J. LUND AND G. A. LOGAN, *J. Gen. Physiol.* 7, 461-71(1925) —When a const. elec. potential of sufficient intensity is applied to *Noctiluca* the protoplasmic films at the surface of the cell break down and release the acid contents from the internal cytoplasm. The process which occurs first at the anode and then at the cathode side of the cell is probably a selective deemulsification or coalescence like that at the surface of an emulsion which has a viscous continuous phase. Nernst's equation,  $\sqrt{I} = k$ , which holds approx. for the threshold stimulation of striated muscle, also applies to the process of anodal coalescence in *Noctiluca*. The thresholds for anodal and cathodal coalescence are different because the semipermeable film at the surface of the cell is asymmetrical with respect to the direction of the current. A possible relation between this phenomenon and the synapse between neurons is pointed out. The threshold intensity of the stimulus is higher for young than for old cells. At least 2 different receptor-affecter mechanisms having a corresponding difference in intensity threshold to an elec. current may occur in the same cell. C. H. R.

Metabolism during embryonic and metamorphic development of insects. D. E. FIVEK, *J. Gen. Physiol.* 7, 527-43(1925). —Insects that deposit their eggs on foliage (*Leptinotarsa decemlineata*, *Circulifer tenax* and *Anasa tristis*) show rates of metabolism as measured by  $\text{O}_2$  intake or  $\text{CO}_2$  output during embryonic development which indicate a short formative period followed by an active extended growth. *Cotinus nitida*

and *Popillia japonica*, which deposit their eggs in the soil, show a great extension of the formative period. A greater amt. of energy change takes place during embryonic development than during metamorphosis. Low respiratory quotients (0.42-0.71) have been obtained during the embryonic and pupal development of insects, resembling those of hibernating forms. Changes from  $pH$  6.8 to 5.9 in the blood of some species have been observed to take place during prepupal and early pupal development. As metamorphosis is completed there is a reversion to  $pH$  6.8. Changes from acid to neutral reaction have also been observed during embryonic development in *Cotinis nitida* and *Hylemya ciliatula*. Metabolism expts. indicate an intensive histolysis during the prepupal period which becomes less intensive during pupal development. C. H. R.

Hydrogen-ion concentration in the blood of insects. R. W. GLASER, *J. Gen. Physiol.* 7, 599-602 (1925).—The  $pH$  of the blood of grasshoppers (*Melanoplus differentialis*) and house flies (*Musca domestica*) ranges from 7.2 to 7.6, that of the cockroach, *Periplaneta americana*, 7.5-8.0. For *Malacosoma americana* and *Bombyx mori* the ranges were 6.4-7.4 and 6.4-7.2, resp. In these species no correlation was observed between blood  $pH$  and age or state of metamorphosis (cf. Fink, preceding abstract).

CHAS. H. RICHARDSON

Temperature characteristic for heart rhythm of the silkworm. W. J. CROZIER AND H. FEDERIGHT, *J. Gen. Physiol.* 7, 565-70 (1925).—"The critical thermal increment for the reaction controlling the frequency of the heart beat in mature silkworms is 12,200 cal. This detn. agrees quantitatively with the increment deduced for other activities of arthropods in which the rate of central nervous discharge is believed to be the controlling element."

CHAS. H. RICHARDSON

The temperature characteristic for pharyngeal breathing rhythm of the frog. W. J. CROZIER AND T. B. STIER, *J. Gen. Physiol.* 7, 571-9 (1925).—"The critical thermal increment for this rhythm is 8800 cal. The frequency probably depends upon a process which is synaptic in locus. The temp. characteristic of this process sharply seps. it from reactions known to be catalyzed by the H ion. It apparently belongs among a group of respiratory reactions."

CHAS. H. RICHARDSON

Pulsation of the contractile vacuole of *Paramecium* as affected by temperature. W. H. COLE, *J. Gen. Physiol.* 7, 581-6 (1925).—"The rate of pulsation of the anterior contractile vacuole of *P. caudatum* under chloretone anesthesia is a logarithmic function of the temp. according to Arrhenius' equation. From 9° to 16°,  $\mu = 25,600$ ; 16-22°,  $\mu = 18,900$ ; 22-31°,  $\mu = 8600$ . At least 3 underlying reactions are responsible for pulsation, and the one which becomes a limiting reaction depends upon the range of temp. Oxidative processes probably do not alone det. the rate of pulsation, but they may be of fundamental importance."

CHAS. H. RICHARDSON

Endocrine glands and bilateral symmetry: forelimb eruption in frog larvae under treatment with thyroid and thymus extracts. C. C. SPRINDEL, *Biol. Bull. Marine Biol. Lab.* 48, 336-45 (1925).

L. W. RIDGES

Crystalline style in gastropods. N. A. MACKINTOSH, *Quart. J. Microscop. Sci.* 69, 317-42 (1925).—"The cryst. style of *Crepidula* is sol. in water, yielding a neutral soln. which is coagulated by boiling or by the addn. of alc. When acidified with dil. AcOH an insol. ppt. forms, indicating mucin. Solns. of style are pptd. by an equal amt. of  $(NH_4)_2SO_4$ . This ppt. dissolved in water and boiled gives a coagulum, indicating globulin. An amylolytic enzyme is present."

G. H. S.

## 12—FOODS

W. D. BIGELOW AND A. E. STEVENSON

Compounds and percentage composition of phosphoric acid in modern prepared foods. C. MASSATSCH, *Chem.-Ztg.* 49, 468-9 (1925).—"Foods contain a considerable amt. of phosphoric acid in combination with org. and inorg. chem. substances, playing an important part in the building up of the body. This is the first of a series of papers in which M. gives the results of analyses made on different brands of prepd. foods on the market. A detailed description of the method of analysis of samples submitted by 1 concern is given, and the results are tabulated.  $P_2O_5$  was detd., and found to be present as protein-, glycerol-, mineral- and lipid- $P_2O_5$ . A sample of skim milk powder was analyzed in a similar way, showing that the prepd. food sample contains the same  $P_2O_5$  compds. (about 50%), and in addn. the lipid- and glycerol- $P_2O_5$  which the milk powder lacked. Results on additional com. brands will be discussed in a later paper. J. C. J."

The chemical and bio-chemical changes in stored food in relation to the nutritive

value of the food. CLARICE M. DUGDALE. *J. State Med.* 32, 564-73(1924).—A discussion of the effect of freezing, chilling and canning on the protein and vitamins of meat and vegetables. Conclusion: the human consumption of an increased proportion of such foods should be without ill effects. H. J. DEUEL, JR.

Is milk a perfect food? J. P. SUTHERLAND. *J. Am. Inst. Homeopathy* 18, 575-83 (1925).—An elaborate discussion of the question with a negative answer. J. S. H.

The determination of fat in milk by the "Neusal" method. RIEDEL. *Molkerei-Ztg* (Hildesheim) 39, 609-10(1925).—R investigated the "Neusal" method (cf. Nothbohn and Angerhausen, *C. A.* 5, 535) with the object in view of adopting it in place of the Gerber  $H_2SO_4$  method to avoid the use of concd  $H_2SO_4$ . The "Neusal" method was found to give satisfactory results provided 9.2 cc. of milk was used instead of 9.7 cc., as specified in the method. The advantages of this method are pointed out. Tables are given. O. L. EVENSON

Cryoscopy as an aid to the identification of neutralized milk. W. KOENIG AND H. KLUGE. *Chem.-Ztg* 49, 437-8(1925).—The cryoscopic method is rapid and easy of manipulation, and the app. is usually present in a food lab. The cryoscopic value of fresh unwatered milk lies between 52.8 and 55.4. Sour milk and milk neutralized with alkali carbonate or bicarbonate have higher cryoscopic values. The method is described. Three samples of milk, each subdivided in fresh, sour and neutralized milk, were examd. for appearance, odor, taste,  $d_{40}^2$ , % fat (Gerber), calcd. fat-free dry substance, acidity degree (Sohrlet-Henkel), cryoscopic value, reaction towards litmus paper, boiling test, alc. test, rosolic acid test, and alizarin test. An abnormal cryoscopic value does not always mean adulteration. J. C. JURJENS

How is the department of food control, especially milk, most efficiently organized? MEZGER. *Chem.-Ztg* 49, 421-3(1925). J. C. JURJENS

The rapid analysis of abnormal milk by the use of the refractometer, by the measurement of catalase, and by the alcoholic-alizarin test. VALENCIEN AND PANCHAUD. *Last* 3, 529(1923); *J. Dairy Sci.* 8, 168-73(1925).—A comparison of the detn. of  $n$  of the  $CaCl_2$  serum, of the detn. of catalase, and of the alcoholic-alizarin test for judging of the suitability of milk for butter and cheese making showed the latter to be the most useful and reliable. The technic of the three tests is described, and a table is given for interpretation of the results of the alcoholic-alizarin test, and equivalence in degrees of acidity. A. PAPINEAU-COUTURE

The effect of the holding method of pasteurization of milk at 63° on the tubercle bacillus. A. MACHENS. *Molkerei-Ztg* (Hildesheim) 39, 779-80(1925).—This is a preliminary paper. The milk from 2 tubercular cows was centrifuged and the sediment was inoculated intramuscularly in guinea pigs. Samples of the same milk were then pasteurized at 63° for 30 min. Portions were then centrifuged and the sediment was inoculated as before. The samples that were not pasteurized gave rise to tuberculous in the pigs. O. L. EVENSON

Relation of water to milk-borne typhoid. C. R. FELLERS AND R. S. DEARSTYNE. *J. Dairy Sci.* 8, 146-67(1925).—An investigation into the longevity of certain bacteria of the typhoid group upon dairy utensils and in water, of the extent of pollution of certain dairy farm water supplies, and of the efficiency of various methods of washing and sterilizing dairy utensils, particularly bottles, clearly shows that considerable precautions must be taken to safeguard the milk supply from the ever-present danger of infection by the water supply, that the use of  $NaOCl$  is equal or superior to steam for the sterilization of milk bottles and dairy utensils, that so called "hot water" washing is inefficient and unsatisfactory from a bacteriological standpoint, and that as a final safeguard the milk should be efficiently pasteurized. A brief review of the literature, with bibliography of 38 references, is given. A. PAPINEAU-COUTURE

The trier compared with the wedge method of sampling tub butter. H. B. ELLENBERGER AND E. S. GUTHRIE. *J. Dairy Sci.* 8, 80-8(1925).—Comparative fat and  $H_2O$  detns. on samples taken by the wedge and trier methods, and also on samples taken after working up the whole tube of butter to a creamy consistency, indicate that the wedge method is the more nearly accurate. For preliminary or "classifying" tests, a diagonal sample may be taken with a trier, and if it gives indications of low fat content a second sample should be taken by the wedge method. A. PAPINEAU-COUTURE

The ripening of cream for butter making. ERICH PUCK. *Molkerei-Ztg* (Hildesheim) 39, 627-8(1925).—Formulas are given for calcg. the optimum acidity for cream to be churned into butter. What in practice has been found to be the optimum acidity in Sohrlet-Henkel degrees for a cream having 24% fat, namely 30, is divided by the % plasma, 76, giving the factor 0.4. O. L. EVENSON

The relation of the fat content of the milk to the fat in the total solids of "Weisz-

lacker" cheese. H. MARTIN. *Milchwirtschaft. Forsch.* 2, 16-21(1924).—In the normal treatment of the cheese with salt, either in the dry form or by means of a salt bath, the fat content is decreased. The max. salt content after 18 weeks is 8 to 10%. The salt penetrates the cheese with equal rapidity, whether dry salt or a salt bath is used, the outer portion having in the former case 7.02% and the inner portion 2.37% salt, while if a salt bath is used the outer part has 5.93% and the inner 2.79% salt. The inner part had slightly more fat than the outer part in both cases. O. L. EVENSON

The testing of flour and baking materials in the laboratory. ARTHUR FORNET. *Chem.-Ztg.* 49, 347-8(1925).—F. discusses the importance of the baking test, and gives a description of a baking oven for the lab. The capacity is 100 g. flour, producing a cake of about 135 g. The baking process lasts 20 min. The vol. of the baked product, which is very important, and which usually takes considerable time, can be detd. in a few seconds. An illustration of the oven and of the exact size of a cake from 100 g. of flour are given. J. C. JURRIJENS

Flour fat and gluten. K. MOHS. *Z. ges. Mühlenwesen* 1, 37-41(1924).—The theory that the color of flour is due to carotin present in the fats, and that bleaching is effected by oxidation of carotin to a colorless O compd. is confirmed and extended. The color of gluten is likewise due to carotin in the fat adsorbed by the gluten-forming proteins. The fat is in a highly dispersed condition, is essential for gluten formation, and cannot be sepd. from the gluten by washing. B. C. A.

Analysis of egg pastes [macaroni]. P. LEONE. *Ann. chim. applicata* 15, 156-9(1925).—Unlike previous methods (cf. *Ricerche sperimentali sulle farine*, Venezia 1909; *Arch. science mediche Torino* 1903, 23; Inchenack, *Z. Nahr. Genussm.* 1(1900); Sendtner, *Ibid.* 1902, 1008; Bandini, *Riv. igiene e sanità pubblica Torino* 1911, 394) which have all proved to be unsatisfactory, a method for determining egg in egg pastes is described, which depends on the differing behavior of egg proteins and those of wheat flour. In principle the method resembles that of Bandini (*loc. cit.*), but the latter gives unreliable results with egg pastes. The procedure is based on the insol. of wheat globulin and glutenin and egg yolk globulin in  $H_2O$  and on the fact that whereas wheat leucosin and gliadin and egg albumin are sol. in  $H_2O$ , only the last gives a ppt. with a dil. soln. of picric acid in citric acid. The egg yolk globulin is in turn characterized by its neutral salt solns. coagulating on boiling. *Procedure.*—Shake 70 g. of finely powd. paste with 100 cc. of  $H_2O$ , let stand 1 hr., decant, filter and add to 5 cc. of the filtrate an equal vol. of a soln. contg. 2% citric and 1% picric acid. A ppt. indicates the presence of egg in the original material. If no ppt. forms, the soln. usually becomes opalescent, which means that egg is absent. A positive test can be obtained with paste contg. 1 egg per kg. of flour. Wash the residue from the original filtration by decantation with  $H_2O$  until the filtrate gives a negative reaction with picric acid, shake the residue with 25 cc. of 10% aq. NaCl, let stand and filter. If the filtrate gives a coagulate on boiling, the presence of egg yolk is certain. If the latter is absent, the NaCl soln. will always remain perfectly clear. Under the conditions above, the vol. of the ppt. with the aq. ext. forms with picric acid after standing 12 hrs. corresponds to about 0.5 division on the Esbac albuminometer for every 2 eggs added per kg. of flour. C. C. DAVIS

The composition of hen eggs in relation to size. E. TSO. *China Med. J.* 39, 136-40(1925).—Hen eggs in China are exceptionally small, averaging about 40 g. in wt. Analyses show that small eggs contain a higher percentage of fat, while the percent of protein does not vary with the size of egg. Small eggs represent a higher calorific value per 100 g. W. H. ADOLPH

#### Determination of N in albuminoid materials (TER MEULEN) 7.

DUKES, CUTHBERT: *The Bacteriology of Food*. London: H. K. Lewis. 190 pp. 7s. 6d.

Milling Chemistry, Questions and Answers. Compiled by S. J. Lawellin and Newton C. Evans. Chicago, Ill.: National Miller. 12S pp.

Slow pasteurization. DE DANSKE MEJERIERES MASENFABRIK A. M. B. A. Danish 34, 235, March 9, 1925. Mech. devices. Cf. C. A. 18, 3658.

Apparatus for continuous sterilization of milk. N. J. NIELSEN. Danish 34, 304, March 23, 1925.

## 13—GENERAL INDUSTRIAL CHEMISTRY

HARLAN S. MINER

The engineer and civilization. FAIRLEY OSGOOD *J. Am. Inst. Elec. Eng.* 44, 705-7(1925)—Presidential address C. G. F.

The new Institute for Applied Chemistry of the University of Erlangen. M. BUSCH *Z. anorg. Chem.* 38, 533-6(1925)—A description of the building F. H.

Industrial heating by oil circulation. J. HARRIS. *Oil Trade* 16, No. 7, 21-2 (1925)—Circulation of hot oil around a jacketed container for heating the contents thereof has proved more satisfactory than the use of steam for this purpose because of the low pressure possible D. F. BROWN

The shipping of substances which evolve oxygen. BRUNO MÜLLER *Chem.-Ztg.* 49, 488-9(1925) E. H.

DANIELS, G. W.: Refrigeration in the Chemical Industry. London A. J. Raymond, 15, Dartmouth St., Westminster, S. W. 1. 141 pp. Reviewed in *Chem. Trade J.* 76, 793(1925)

MARTIN, GEOFFREY, et al.: Industrial and Manufacturing Chemistry. Vol. 2, Pt. 2. Inorganic. London C. Lockwood & Son. 498 pp. 28s.

RASSOW, BERNHOLD: Die chemische Industrie. Gotha: Flamberg Verlag. 131 pp. R. M. 3 50; bound R. M. 4.

Weltadressbuch der chemischen Industrien. 2 Vols. 5th ed. Vol. 1. Deutschland u. Deutsch-Oesterreich. 776 pp. R. M. 20 Vol. 2. Die aussersdeutschen Lander 928 pp. R. M. 25. Berlin: Union, Zweigniederlassg.

## 14—WATER, SEWAGE AND SANITATION

EDWARD BARTOW AND G. C. BAKER

Index of analyses of natural waters of the U. S. W. D. COLLINS AND C. S. HOWARD. U. S. Geol. Survey, *Water-Supply Paper* 560C, 53-85(1925). L. W. RIGGS

The limitation of losses in measuring water on a large scale. VOLLMAR AND BAESE *Gas u. Wasserfach* 68, 355-60(1925).—A discussion, with curves and tables, of the accuracy of various devices for the measurement of large vols. of  $H_2O$  W. B. P.

Water treatment and softening plant at Springfield, Ill. C. S. TIMANUA. *J. Am. Water Works Assoc.* 13, 1630-7(1925)—The hardness consists of 60%  $Ca(HCO_3)_2$ , 25%  $Mg(HCO_3)_2$ , and 15%  $MgSO_4$ . Lime will be used to remove all the  $Ca$  hardness and part of the  $Mg(HCO_3)_2$ , the other impurities being ignored. Alum will be added when necessary, after clarification and sedimentation, the water, as it leaves the settling basins, will be carbonated to prevent after-deposits. D. K. FRENCH

Water filtration plant at Chippawa. C. G. REID AND D. H. FLEMING. *Can. Eng.* 48, 285-7(1925)—A small plant with a horizontal mesh filter is described. C. C. R.

Vest station—Charlotte water works. E. C. McCONNELL. *Pub. Works* 56, 110-4(1925)—An 8 million gallon capacity filter plant with a novel rate controller and original filter bottom is described. C. C. R.

Methods of water purification in Providence, R. I. J. W. BUGBEE. *Eng. Contr.* 62, 829-32(1925)—The supply is filtered through slow sand filters at a rate of 2.5 million gallons per acre per day, treated with 50 to 100 lbs. of lime and 3 to 8 lbs. of  $Cl$  per million gallons. Lime treatment reduced the av. amt. of  $Pb$  found in the tap water from 0.29 to 0.05 p.p.m. C. C. R.

Treatment and filtration of water. H. W. CLARK. *Eng. Contr.* 63, 291-4(1925).—Observations and tests on loaded slow sand filters are described. C. C. R.

Size and depth of sand for filters. C. M. DALEY. *Eng. Contr.* 62, 827-8(1924).—A depth of 24 in. of sand graded from 0.38 mm. to 1.0 mm. in diam. will give satisfactory results. The effluent after washing was first clear, then became turbid for about 45 min. running at 1/4 rate; after which it became clear and remained so after raising the rate to 3 million gallons daily until the tests were concluded at a 10-foot loss of head. The agar count in the effluent roughly follows the same changes as the turbidity. C. C. R.

Municipal water supply filter sand. W. M. WRIGHT. *Can. Eng.* 48, 377-8 (1925).—The requirements and specifications for filter sand are given and the method of mining and prepg. the sand is described. C. C. R.

- A portable water-testing set. HARTWIG KLUT. *Gas u. Wasserfach* 68, 369-70 (1925).—A description of a com testing equipment WM. B. PLUMMER  
Applying copper sulfate. ANON. *Eng. Contr.* 63, 125-6; *Pub. Works* 56, 55 (1925).—A dose of 0.05 p.p.m. applied on 3 days from a spraying machine was effective. C. C. R.

Water supplies and typhoid fever. C. A. HOLMQUIST. *Can. Eng.* 48, 385-6 (1925).—Raising the purity standard of water in New York State has reduced the typhoid rate. C. C. R.

Isolation of the colon group in water. N. J. HOWARD AND R. E. THOMPSON. *Can. Eng.* 48, 413-7(1925).—Studies with brilliant green bile broth indicate that it is slightly inhibitive and its use for the presumptive test is not recommended. The possibility of its use in confirming the colon group from presumptive lactose broth tubes in place of eosin methylene blue plates is suggested. A description of colonies isolated from eosin methylene blue agar with their carbohydrate reactions is given C. C. R.

Activated sludge plants at Houston. J. V. McVEA. *Can. Eng.* 48, 323-4(1925).—Operating data show that the plants are producing a good effluent. C. C. R.

Sewage disposal plant for Milwaukee. T. C. HATTON. *Can. Eng.* 48, 365-6 (1925).—A description of the method of treating the sludge is given. C. C. R.

New Jersey sewage disposal studies. ANON. *Pub. Works* 56, 101-5(1925).—The results of chem and bacteriol analyses on operating and resting Imhoff tanks, and the fauna of tanks, sprinkling filter and filter beds are given C. C. R.

Fitchburg sewage treatment plant. ANON. *Pub. Works* 56, 8-9(1925).—The operation of the Imhoff tanks, trickling filters, secondary tanks and sludge beds is described and cost data are given. C. C. R.

Some observations on sewage treatment in Scandinavia. G. PEEL HARVEY. *Eng. Contr.* 63, 311-7(1925).—Experiences with septic tanks, trickling filters and with the treatment of waste from a yeast plant are described. C. C. R.

Imhoff tank discussion. ANON. *Pub. Works* 56, 10-11(1925).—Attempts to correct foaming in tanks are described. C. C. RUCHHOFF

KOPP, ANDRÉ: Les eaux minérales de Soultzbach (Haut-Rhin). Étude historique physico-chimique, et thérapeutique. Schlettstadt: Soc. als. d'ed. Alsatia 70 pp.

## 15—SOILS, FERTILIZERS AND AGRICULTURAL POISONS

J. J. SKINNER

An answer to the work: "Do relations exist between the colloidal portion of the soil soluble in hydrochloric acid and the fertility of the soil and its need for fertilizer?" by R. GANSSSEN (Gans). B. TACKE AND T. ARND. *Internat. Mitt. für Bodenk.* 14, 155-7(1924); cf. C. A. 19, 371.—Exception is taken to the theory of Ganssen that those soils whose colloidal material sol in HCl shows the mol. relationship 3 or more mol. equivs. of  $\text{SiO}_2$  combined with 1 mol. equiv. of  $\text{Al}_2\text{O}_3$  and with more than 1 mol. equiv. of total bases, are alk. and do not require fertilizer on the ground that certain marsh soils showing that relationship are acid because of their content of acid humus, and because they respond to potash or phosphoric acid I. A. DENISON

Molecular relationship, soil reaction and need of fertilizer. R. GANSSSEN (GANS). *Intern. Mitt. für Bodenk.* 14, 158-70(1924).—A close relationship exists between the reaction of a soil, the quantity of bases absorbed, and the ratio,  $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ :base, in the colloidal portion of the soil sol. in HCl I. A. DENISON

Study of soil acidity and lime deficiency. V. VINCENT. *Ann. sci. agron.* 41, 1-13, 122-34(1924); *Expt. Sta. Record* 52, 21-2.—Studies are reported showing that free lime occurring in the soil in the presence of free  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  is combined according to the formula  $\text{SiO}_2 \cdot 3\text{CaO}$  or  $\text{Al}_2\text{O}_3 \cdot 3\text{CaO}$ , with the possible formation of a sol. aluminate  $\text{Al}_2\text{O}_3 \cdot 3.5\text{CaO}$ . Where the  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  occur as Al silicate, the reactions are the same as where these materials occur alone. Ferric hydroxide does not combine with the lime, but the process is one of lime adsorption, varying in proportion according to the lime-ferric hydroxide ratio. Such adsorption is diminished in the presence of free  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ . Where the lime is combined with carbonic acid the  $\text{SiO}_2$  is inactive, but the  $\text{Al}_2\text{O}_3$  combines according to the formula  $\text{Al}_2\text{O}_3 \cdot 3\text{CaO}$ .  $\text{Ca}(\text{HCO}_3)_2$  in the presence of free and sol.  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  ppts. the  $\text{SiO}_2$  without combining with it, while the  $\text{Al}_2\text{O}_3$  remains in soln. These results are taken to indicate that in the soil lime combines solely with  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , in addn. to org. matter and mineral salts, and is adsorbed in very

small quantities by ferric hydroxide. In fact,  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  are considered to be of primary importance in the fixation of lime in the soil. Studies of the influence of solns. of soda, lime, and  $\text{Ca}(\text{HCO}_3)_2$  on ground pebbles showed that coarse pebbles in their natural state in the soil do not possess acid properties, and that free or combined bases react with the silicates. Studies of the action of lime and the bicarbonates of Ca and Na on blue clay demonstrated that clay is one of the important factors in the mineral acidity of soils. H. G.

Dispersing power of alkali in soil. A. DE DOMINICIS. *Ann. Scuola super. agr. Portici* [2] 17, 22 pp. (1922); *Expt. Sta. Record* 52, 21.—Studies are reported which showed that electrolytes influence the tendency of soil colloids to change their state. Also progressive dilns. of neutral salts have an influence contrary to dispersion, which is considered to govern the formation of absorptive compds. that are insol. in the presence of electrolytes. Const. concns. of alkali compds. favor dispersion, which is attributed to the influence of the OH ion. This action is caused by the electronegative charge of the soil colloids, particles having the same charge repelling each other. The OH ions determine both the sign and amt. of the charge. Therefore the tendency toward dispersion and major subdivision of the colloids increases with the concn. of active OH ions. The active OH ions which are capable of combining with the colloidal particles are able to influence a certain no. of particles of each mass of soil colloids, which coincides with the max. of dispersion and with the stability of the disperse state. Beyond this max. the alkalis tend to favor coagulation. This is due to the activity of the ion having an elec. charge opposite to that of the OH ion and the charge of the colloidal particle. H. G.

Losses of ammonia from soil by volatilization. G. R. CLARKE AND C. G. T. MORRISON. *Nature* 115, 423-4 (1925).—Preliminary expts. show that during simultaneous desiccation and aeration, considerable amts. of  $\text{NH}_3$  are volatilized from soil. B. C. A.

Analyses of soils of the Cattavia Valley, Island of Rhodes. A. FERRARA AND M. SACCHETTI. *Agr. Colon. [Italy]* 17, 333-7 (1923); *Expt. Sta. Rec.* 52, 18.—Phys., mech., and chem. analyses of 5 samples of soils typical of the valley lands in the southwestern extremity of the Island of Rhodes are presented and briefly discussed. H. G.

Effect of season on nitrification in soils. F. LÖNNIS. *Centr. Bakt. Parasitenk. II Abt.* 58, 207-11 (1923).—This is a criticism of Schonbrunn's conclusions (*C. A.* 17, 174). L. contends that there is a seasonal effect in nitrification. JULIAN H. LEWIS

Comparative effects of carbon disulfide, dichloroethylene, tetrachloroethylene and tetrachloroethane in soil disinfection. SCHWARZEL. *Centr. Bakt. Parasitenk.* 60, 316-8 (1923).— $\text{CS}_2$ ,  $\text{C}_2\text{H}_2\text{Cl}_2$ ,  $\text{C}_2\text{Cl}_4$  can increase the yield from soil while  $\text{C}_2\text{H}_2\text{Cl}_4$  is injurious. JULIAN H. LEWIS

World-wide production and need of the more important potash, phosphoric acid and nitrogen fertilizers before and after the World War. P. KRISCHKE. *Chem.-Ztg.* 49, 453-5, 486-8, 506-8 (1925). E. J. C.

The use and preparation of concentrated fertilizers. WM. H. ROSA. *Trans. Am. Electrochem. Soc.* 48 (preprint) (1925); cf. *C. A.* 19, 555.—The conception of "concentrated fertilizers" originated at the U. S. Bur. of Soils. The prepn. of  $\text{NH}_3$ , phosphate as well as other concd. materials requires the use of free phosphoric acid. The most concd. mixts. contain  $\text{NH}_3$ , phosphate, K phosphate and  $\text{KNO}_3$ . There is no known single chem. compd. contg. N, P and K. Brief accounts are given for the manuf. of  $\text{NH}_3$ , phosphate, K phosphate,  $\text{KNO}_3$ , urea and  $\text{NH}_4\text{NO}_3$ . Field tests with concd. fertilizers are now being made by the Bur. of Soils. The concd. fertilizers so far prepd. contain neither sulfates nor Mg salts. It may develop later that certain soils require S and Mg and if so, these can be incorporated as gypsum and dolomite.  $\text{NH}_3$ , urea, nitric and phosphoric acids are products, or by-products of electrochem. industries. Conc'd. fertilizers save on freight and tend to conserve org. ammoniates. C. G. F.

The development of fertilizer practice. R. O. E. DAVIS. *Trans. Am. Electrochem. Soc.* 48 (preprint) (1925).—Lately there has been a decided trend towards the prepn. of concd. fertilizers and the establishment of the fertilizer industry on a strictly chem. basis. The elimination of fillers means a great saving in freight charges. Most of the fertilizer now consumed in this country is consumed in the east and southeast, but with the introduction of conc'd. fertilizers and consequent lower freight rates, the territory is bound to be extended. C. G. F.

The development of volatilization methods for the manufacture of phosphoric acid. K. D. JACOB. *Trans. Am. Electrochem. Soc.* 48 (preprint) (1925).—A large portion of the phosphoric fertilizer is still made by the old Liebig-Lawes methods. Most of our soils require more P than K and N. To meet the increasing cost of transportation, the phosphate fertilizers must hereafter be in concd. form such as K,  $\text{NH}_3$ , or Ca phosphates.

Heretofore 80% of the "phosphate fertilizers" were of little or no fertilizer value. In the volatilization process for the production of the liquid phosphoric acid, as carried out commercially at Anniston, Ala., a mixt. of phosphate rock, sand and coke is heated to 1600° in an elec. furnace. A Cottrell precipitator is used to recover the volatilized  $P_2O_5$ . A recent modification of this process consists in the substitution of an oil-fired furnace for the elec. furnace. It is difficult to attain 1600° in fuel-fired furnaces. However, recent tests indicate that the phosphate rock-coke-silica mixt. will react at as low a temp. as 1200°. This research is still in progress. C. G. F.

The conversion of phosphorites into superphosphates. S. A. MIKHNO. *Khim. Promuishlennost'* 3, 19-21 (1925).—The manufacture of superphosphates in Russia at the present time. H. BERNHARD

Special reports prepared under the direction of the subcommittee on insecticides and appliances, committee on policy. Report on oil emulsions. J. J. DAVIS, A. J. ACKERMAN, W. W. YOTHERS AND L. HASEMAN. *J. Econ. Entomol.* 18, 410-3 (1925).—The boiled lubricating oil emulsion is considered the best. Formula: lubricating oil 1 gal., K fish oil soap 1 lb., water  $\frac{1}{4}$  gal. Hard waters may require as much as 2 lbs. soap to maintain the emulsion. The following cold-mixed emulsions have been found satisfactory under certain conditions: (1) Oil 1 gal.,  $CaSO_4$   $\frac{1}{4}$  lb.,  $Ca(OH)_2$   $\frac{1}{4}$  lb., water  $\frac{1}{2}$  gal. (2) Oil 1 gal., Ca caseinate 2-4 oz., water  $\frac{1}{2}$  gal. (3) Oil 1 gal.,  $FeSO_4$   $\frac{1}{4}$  lb.,  $Ca(OH)_2$   $\frac{1}{4}$  lb., water 1 gal. (4) Oil (neutral lubricating) 91%, K fish oil soap (contg. 30% moisture) 5%, crude cresylic acid 4%. The soap and cresylic acid are mixed together then stirred with the oil without beating. A lubricating oil having the following properties should be used: viscosity 90-250 sec. at 100° F. (Saybolt), volatility less than 2%, sp. gr. 0.87-0.93 (20°). These are the extreme limits. Best results in scale control will probably be obtained with an oil which falls within the following limits: viscosity 180-220 sec. at 100° F., volatility less than 1%, sp. gr. 0.88-0.91 at 20°. Boiled emulsions were considered equally as effective as cold-mixed emulsions, but the former are believed to be more stable than the cold-mixed. Both kinds are very adhesive and have good spreading qualities. The boiled emulsion mixes well with Bordeaux mixt., Pb arsenate and nicotine but not with lime-sulfur soln. The cold-mixed emulsion will mix with lime-sulfur. When used with weak Bordeaux mixt. (1/2-1/2-50) an emulsion may be mixed with most hard waters. The insecticide uses of oil emulsions are discussed; also their effects on plant diseases and on foliage. What is the status of spreaders in our spray program? L. A. STEARNS, R. H. ROBINSON, R. H. SMITH AND L. CHILDS. *Ibid* 413-5.—The questions are discussed and a no. of subjects for research are indicated. Results obtained by the use of calcium cyanide. E. N. CORY, J. W. MCCOLLOCH AND W. P. FLINT. *Ibid* 415-6.—The use of  $Ca(CN)_2$  as an insecticide is discussed. Insecticide machinery. F. H. LATHROP, P. GARMAN, B. B. FULTON AND R. H. SMITH. *Ibid* 416-20.—A consideration of the various types of insecticide appliances. CHAS. H. RICHARDSON

A method of computing the effectiveness of an insecticide. W. S. ABBOTT, *J. Econ. Entomol.* 18, 265-7 (1925).—The formula used is  $(x - y)100/x = \%$  control, in which  $x$  is the % of insects living in the control, and  $y$  the % living in the treated plot. C. H. R.

An investigation of sulfur as an insecticide. A. HARTZELL AND F. H. LATHROP. *J. Econ. Entomol.* 18, 267-79 (1925).—A lab. and field study. Atms. contg. the volatile products of lime-S soln. killed San Jose scale (*Aspidiotus perniciosus*) especially the young. Lime-S soln. does not appreciably soften or dissolve the scale covering. Three new S insecticides are reported: (1)  $CS_2$ -S emulsion, made by emulsifying  $CS_2$  which contains dissolved S in water with soap. This was a promising spray for *Psylla pyri* and San Jose scale. (2) S-naphthalene dust prepd. from S flowers dissolved in melted naphthalene, by rapidly chilling the soln. and reducing the solid to a dust. It was used against the red spider and aphids in greenhouses. (3) Colloidal S prepd. by passing S fumes into aq. solns. of soap or glue. This was effective in the control of insects and apple scab. CHAS. H. RICHARDSON

Fish oil—An efficient adhesive in arsenate of lead sprays, and results with other substances used. C. E. HOON. *J. Econ. Entomol.* 18, 280-1 (1925).—Lined oil was the best for this purpose, but fish oil was nearly as good, and cheaper. C. H. R.

Electric charges of arsenical particles. W. MOORE. *J. Econ. Entomol.* 18, 282-6 (1925).—When suspended in water, most of the arsenicals at present manufactured show a negative or no elec. charge. They offer no special resistance to removal from foliage by rain or dew. The common arsenicals may be prepd. in such a manner that they will have a positive elec. charge when wet, due to the presence of an adsorbed positive ion. These will strongly adhere to leaf surfaces which are electronegative,

and will resist rains and dew. Such a positively charged Ca arsenate has been made. The common arsenicals may acquire a positive or negative static charge when dusted on plants. Such a charge will aid in evenly distributing the material over the plant, but will not prevent it from being washed off. CHAS. H. RICHARDSON

Miscible oils and oil emulsions. J. G. SANDERS. *J. Econ. Entomol.* 18, 287-92 (1925).—A general treatment of the subject. C. H. R.

The fatty acids as contact insecticides. E. H. SIEGLER AND C. H. POPENOE. *J. Econ. Entomol.* 18, 292-9 (1925); cf. *C. A.* 19, 1174.—The toxicity of soaps to insects is probably due to the free fatty acids present in their soaps. The lower normal satd. monocarboxylic acids have no marked toxicity to insects, but the higher members are decidedly toxic. Practical toxicity begins with caproic acid. Caprylic, capric and lauric acids, and to a lesser extent myristic acid, also are toxic. Nonoic acid, an odd-C acid, is about equal to lauric. The fatty acids probably penetrate the body wall and tracheae in the crystalloid state and exert a hemolytic action on the blood and body cells. The effect of these acids on plants when applied in sprays is variable, depending upon the species of plant, but apple foliage is not injured by concns. which are toxic to apple aphids. The free fatty acids are more toxic than their salts with alkali metals and  $\text{NH}_3$ . The best com. source is, "double distd. coconut fatty acids." This mixt. is made into a stock soln. as follows: Coconut fatty acids 200 cc., benzene or gasoline 200 cc., glue (granular) 100 g., water 525 cc. This soln. is dild. for spraying purposes. Coconut fatty acids compare favorably by wt. with com. 40% nicotine sulfate soln. To insure the best results all the insects must be wetted since the vapors are not toxic. Six species of aphids, some other insects and *Acarina* were used in these expts., which are considered to be preliminary. CHAS. H. RICHARDSON

A newly recommended fumigant, ethyl acetate in combination with carbon tetrachloride. E. A. BACK AND R. T. CORTON. *J. Econ. Entomol.* 18, 302-8 (1925).—This mixt. is satisfactory as a household fumigant if used in a tight container. It is non-explosive and non-inflammable and has an agreeable odor. It is also effective for threshed grain in cars, but less so for grain in cribs. C. H. R.

The fumigation of "balled" nursery stock. B. R. LEACH AND W. E. FLEMING. *J. Econ. Entomol.* 18, 362-7 (1925).—Heretofore nursery stock has not been successfully fumigated, because the foliage has been injured by the gas. By submerging the aerial portion of the plant in water, it is possible to fumigate the roots and their attached soil with  $\text{CS}_2$ . Methods are given. C. H. R.

Emulsifying agents as an inhibiting factor in oil sprays. E. R. DE ONG AND H. KNIGHT. *J. Econ. Entomol.* 18, 424 (1925).—The insecticidal value of refined lubricating petroleum oils resides in their mech. properties rather than in any inherent toxicity. Any oil which is sufficiently viscous to form a non-volatile film is probably effective. Anything which tends to prevent the formation or retention of this film inhibits the action of the oil. To insure best insecticidal results, an oil should be applied as nearly as possible in the form of a mech. mixt. of oil and water. C. H. R.

The distribution of an insecticide made visible. A. C. MORGAN AND R. G. MEW-NORNE. *J. Econ. Entomol.* 18, 299-302 (1925).—A mixt. of Pb arsenate and phenolphthalein was dusted on tobacco foliage. Prints of the leaves were taken on paper impregnated with NaOH soln. The distribution of the Pb arsenate was thus made evident. C. H. R.

A colorimetric method for showing the distribution and quantity of lead arsenate upon sprayed and dusted surfaces. C. C. HAMILTON AND C. M. SMITH. *J. Econ. Entomol.* 18, 502-9 (1925).—Pb arsenate suspended in water is sprayed upon foliage. The sprayed surface is pressed between blotting paper satd. with 2% NaOH soln. The dissolved Pb is adsorbed by the paper and does not spread. It is then made visible by exposure to  $\text{H}_2\text{S}$ . The thin films of  $\text{PbS}$  obtained by this method are yellow, amber, brown or rarely black, depending upon the quantity of Pb present. The method shows the distribution of Pb arsenate and roughly the amt. present. For more accurate work, the Pb arsenate may be dissolved from the leaf with 1% NaOH soln., the resulting soln. being treated with  $\text{H}_2\text{S}$  with 0.1% gum arabic added to prevent coagulation and pptn. Comparison is made with a standard in a Nessler or test tube. Detns. of the amt. of Pb arsenate on peach foliage after spraying with mixts. contg. various kinds of spreaders are given. The effect of washing is brought out. CHAS. H. RICHARDSON

A preliminary report on the preparation of insecticide emulsions with a colloidal clay. L. L. ENGLISH. *J. Econ. Entomol.* 18, 513-5 (1925).—The use of colloidal clay (bentonite) as an emulsifier for kerosene, red engine oil, paraffin oil and furfural is described. C. H. R.

Cold-process emulsions. W. W. YOTHERS. *J. Econ. Entomol.* 18, 545-6 (1925).—

Three formulas are given for the prepn. of emulsions of lubricating oils. (1) kaolin 2 $\frac{1}{2}$  lbs., oil 2 gal., water 1 gal.; (2) ground glue 1 lb., other ingredients the same; (3) skimmed milk powder 14-16 oz., other ingredients the same. All are mixed without heating.

C. H. R.

Some spray tests with oil emulsions. L. I. HUBER. *J. Econ. Entomol.* 18, 547-8(1925).—A brief discussion of the effect on emulsification of the ratio of oil, soap and water, the degree of mech. mixture, and the amt. of heating.

C. H. R.

Cupric sulfate in agriculture. ERCOLE CERASOLI. *Giorn. chim. ind. applicata* 6, 536-7(1924).—C. suggests the use of Cu in minimal amts. in spraying compds., and in powder form rather than in liquid form.

ROBERT S. POSMONTIER

Fertilizing value of lime sludge from sulfate pulp manufacture (KLEIN) 23. CaCN<sub>2</sub> (REMY) 18.

CLARKE, G. R. Soil Acidity and Its Relation to the Production of Nitrate and Ammonia in Woodland Soils. Oxford: The Clarendon Press, 27 pp. Reviewed in *Bull. Imp. Inst.* 23, 128(1925).

## 16—THE FERMENTATION INDUSTRIES

C. N. FREY

The manufacture of alcohol from horse chestnuts. RUDOLF VADAS. *Chem.-Ztg.* 49, 372(1925).—Horse chestnuts contain, when dried to 12% H<sub>2</sub>O, 46-49% starch. After removal of the glucoside the starch is converted to sugar and fermented. 100 kg. dry chestnuts yield 23-25 l. alc.

C. N. FREY

Conversion of  $\alpha$ -hop-bitter acid (humulone) during boiling in aqueous solution. W. WINDISCH, P. KOLBACH AND H. GROHN. *Wochschr. Brauerei* 41, 281-3, 289-92, 299-302(1924).—Expts. were made on the decompn. of humulone by boiling under different conditions of H-ion concn. Humulone was detd. by pptn. as Pb salt in 80% MeOH soln., a series of detns. being made to verify this method. The percentage decompn. of humulone on boiling for 1 hr. in solns. of decreasing H-ion concn. decreased to a min. of about 20% at about  $p_H$  6.7 and then increased rapidly to 45% at  $p_H$  8.6. The min. decompn. corresponding approx. to abs. neutrality ( $p_H$  7) may be due to the influence of the H-ion concn. on the ratio of colloidal to molecularly dissolved humulone in the soln. The rate of decompn. of humulone when boiled for a prolonged period under const. H-ion concn. ( $p_H$  7.25) decreased slightly because of the increase in H ion concn. When the concn. of the buffer soln. was increased, the rate of decompn. became more constant and the curve corresponded to that of a unimol. reaction.

B. C. A.

The mechanism of the action of cupric compounds in the treatment of cryptogamic diseases of wine. HENRI BLIN. *La nature* 53, i, 93 Suppl.(1925).—A review, with special reference to the work of Villedieu (*C. A.* 16, 263, 983, 1829, 2005, 2194, 2753) and of Raphael (*Bull. soc. linnéenne Lyon* 1899).

C. C. DAVIS

Mashing apparatus. O. E. OHLSSON. Swed. 58,454, April 1, 1925. Mech. features.

## 17—PHARMACEUTICAL CHEMISTRY

W. O. EMERY

Chinese camphor and camphor oil. P. L. BRYANT. *China J. Science & Arts* 3, 228-34(1925).—Chinese camphor is identical with that from Formosa, but Chinese camphor oil differs from Formosan camphor oil. The crude methods still used employ small iron stills. No adequate analysis of Chinese camphor oil has ever been made. This oil and the polyterpenes obtained from it offer great possibilities to the investigator.

W. H. ADOLPH

Chinese inorganic materia medica. B. E. READ AND C. O. LEE. *China Med. J.* 39, 23-32(1925); cf. *C. A.* 19, 700.—The following materials of Chinese origin prepd. after the formulas of the ancient *Pen Tsao* satisfy pharmacopeial standards: copper sulfate, ferrous sulfate, sodium sulfate, alum, kaolin, mercury, arsenic, calamine.

W. H. ADOLPH

Chemical analysis and physiological properties of fuh-ling. B. E. READ AND S.

Y. WONG. *China Med. J.* 39, 314-20(1925).—Fuh-ling, or *Pachyma cocos*, differs slightly from the American "Indian bread." It analyzes 84.20% pachymose, which is proved to be a simple anhydride of glucose. The drug has distinct nutritive values, but the old assumption that it possesses diuretic and sedative properties is not confirmed.

W. H. ADOLPH

Preparation of medicinal vaseline from technical vaseline and from "masut" containing paraffin wax. A. DEMCHENKO AND A. VOONOV. *Nestjane i slancevoj Chozjajstvo* 7, 116-9(1924).—The technical vaseline or masut is dissolved in benzine, shaken with charcoal (preferably Zelinski's activated charcoal), decanted and fractionated. The process is cheaper than that of filtration through charcoal, and a further cheapening may be effected by using alumina from North Caucasus instead of charcoal.

B. C. A.

Essential oils. SCHIMMEL & Co. *Rep. Schimmel & Co.* 1924, 1-236.—Bay oil had a variable phenol content from 35 to 60%. Citronella oil: this statement of de Jong and van Harpen (*C. A.* 17, 2471) that the viscosity of the oil varies inversely with the citronellal content is not confirmed; the detg. factor is probably the degree of resinification. Jaborandi leaf oil the characteristic odor is probably due to a ketone; a sample of oil having  $d^{15}_4$  0.8694,  $\alpha_D^{20} +0^\circ 54'$ ,  $n^{20}_D$  1.45442, acid no. 6.72, Ac no. 7.65, on extn. with  $\text{NaHSO}_4$  yielded a methyl nonyl ketone, b.<sub>760</sub> 231.5-232.5°,  $d^{15}_4$  0.8297;  $\alpha_D$  0,  $n^{20}_D$  1.42835, Ac no. 11.7; the lower-boiling fractions afforded a hydrocarbon, b. 162-6°,  $d^{15}_4$  0.8519,  $\alpha_D +17.4^\circ$ ,  $n^{20}_D$  1.46757, which absorbs HCl to give a liquid hydrochloride, while the higher fractions afforded a hydrocarbon, m. 27-28°, previously described. Oil from *Monarda fistulosa*: on steam distn. the plant yielded 0.3% of a deep reddish brown oil,  $d^{15}_4$  0.9219; 5% KOH soln. extd. about 30%, chiefly carvacrol, traces of thymol, and probably some thymoquinol. Oil from *Monodora myristica* obtained from West African seeds gave 5.06% of a pale yellow oil with an odor of phellandrene,  $d^{15}_4$  0.8311,  $\alpha_D$  86° 20',  $n^{20}_D$  1.47613, acid no. 0.4, Ac no. 6.5; after fusion of the nitrite (102°), it gave  $\beta$ -phellandrene; it also seemed to contain some cineole. A vetiver oil from Java had a powerful odor and dark brown color,  $d^{15}_4$  0.9926-1.0444,  $\alpha_D +20^\circ 50'$  to  $+41^\circ 40'$ ,  $n^{20}_D$  1.51880-1.53020, acid no. 9.3 to 28, Ac no. 5.6-20.8, after acetylation 107.3-151.2; some "light oils" occasionally present had  $d^{15}_4$  0.9853-0.9944,  $\alpha_D$  14° 25' to 24° 10',  $n^{20}_D$  1.52430-1.52604, acid no. 7.5 to 11.2, Ac no. 7.5-14.9, after acetylation 102.7 to 108.3. Specimens of (presumably synthetic) menthol had m. p. 32-36.5°,  $\alpha_D -39^\circ 55'$  to  $-41^\circ 30'$ , and are probably made from piperitone. The details given by Reclaire (*C. A.* 17, 3402) for the identification of esters of non-volatile acids in oils are confirmed, but acids slowly volatile in steam, such as lauric acid, are likely to be overlooked. The gusl. tests of Bennett and Garratt (*C. A.* 18, 566) are useful, but in negative tests the acid no. should be detd.

B. C. A.

Oil from *Santolina chamaecyparissus*, L. L. FRANCESCONI AND P. SCARAFIA. *Ris. ital. essenze e profumi* 6, 76-9(1924).—The oil, which is contained chiefly in the epidermis and palisade cells of the leaves, is obtained by steam distn. in a yield of 2.6-13.2%. It has  $d^{15}_4$  0.8704-0.8732 [ $\alpha_D$ ] =  $-11.74^\circ$  to  $-16.43^\circ$ , and b. 176-250°, leaving a black pitch-like residue. The phys. const. of fractions obtained by distg. the oil at 15-20 mm. (b. 94-111°) are tabulated. The residue (10%) of this distn. was converted by steam into a yellow resin,  $d^{15}_4$  0.9538 [ $\alpha_D$ ] =  $-18.57^\circ$ , and an oil,  $d^{15}_4$  0.9344 [ $\alpha_D$ ] =  $32.21^\circ$ .

B. C. A.

Some medicinal extracts. QUENTINO MINGOIA. *Ann. chim. applicata* 15, 95-116 (1925).—The phys. and chem. properties of representative samples of the aq. ext. of rhubarb (*Rheum officinale*), the dried aq. ext. of ratany (*Krameria triandra*) and the Et<sub>2</sub>O ext. of cubeb (*Peper cubeba officinalis*) were studied in great detail in an attempt to det. the validity and the significance of the various tests and properties described in the Italian, French, German and U. S. pharmacopoeias. The properties of the exts. and the numerous tests which serve to identify them and as criteria of their therapeutic value are given in detail. As a result of the tests, the following properties are considered to be characteristic of the 3 active exts. (in the order above) when they are of satisfactory quality: consistency, soft, spongy friable granules, semifluid; color, red-brown, red-brown, green-brown; taste, bitter but pleasant, bitter and styptic, burning; odor, aromatic and characteristic, slightly aromatic, like juniper; after exposure to air, pillular, unaltered, decompd.;  $\text{H}_2\text{O}$ , sol. in cold and extremely sol. in hot, slightly sol. in cold and sol. in hot, insol. in cold and slightly sol. in hot, all 3 with an acid reaction; 95% EtOH, slightly sol. in hot, insol. in cold and slightly sol. in hot, sol. in cold and hot;  $\text{C}_6\text{H}_6$ , petr.-ether, insol., insol., sol.; concd.  $\text{H}_2\text{SO}_4$ , sol. with intense red-brown color,

sol. with blood-red color, sol. with red-brown color; concd. HCl, sol. with crimson color, slightly sol. with golden color, slightly sol. with blood-red color;  $\text{AgNO}_3 + \text{HNO}_3$ , turbidity sol. in  $\text{NH}_4\text{OH}$ , opalescence sol. in  $\text{NH}_4\text{OH}$ , nothing;  $\text{NH}_4\text{OH}$ , blood-red color, blood-red color, nothing;  $\text{FeCl}_3$ , intense green with ppt., ppt. first green then maroon, nothing;  $\text{Pb}(\text{OAc})_2$ , rust-colored ppt., white ppt. becoming red, turbidity; basic  $\text{Pb}(\text{OAc})_2$ , brown ppt., lilac ppt., bluish ppt.; Fehling soln., reduction when hot, reduction when hot, delayed reduction when hot; Fröhde reagent, brown-green ppt., brown ring between the layers, nothing; Wagner reagent, red-brown ppt., sienna-colored ppt., nothing; Mayer reagent, malaga-grape-colored ppt., nothing; picric acid, yellow turbidity, nothing, nothing. The 3 exts. examd. also showed the following results expressed as % of the ext.; residue at  $100^\circ$ , 78.10, 81.88, 71.93; ash, 7.17, 3.76, 0.39; free acids expressed as NaOH, 10.57, 11.06, 0.08; active principle, 16.85, 1.79, 2.30.

C. C. DAVIS

Researches on the essential oils extracted from the aromatic plants of Sardinia. I. E. PUXEDDU. *Ann. chim. applicata* 15, 159-70 (1925).—As the beginning of a systematic study of the essential oils of Sardinian plants, the *Rosmarinus officinalis* Lin., *Lavandula stoechas* Lin., *Teucrium polium* Lin., *Artemisia arborescens* Lin., and *Thymus capitatus* Lk. were distd. and the phys. and chem. consts. of the oils detd. The plants were distd. with  $\text{H}_2\text{O}$  with direct heat and the oil and  $\text{H}_2\text{O}$  distillates sep'd. The aq. distillate was used for the subsequent distn. so that any emulsified oil would be recovered and the yields thereby increased. Some of the oils were dark or became so when exposed to light and air, the color varying with different lots of the same plant. They were therefore redistd. in a current of steam, which left a resinous residue and gave distn. products which were of lighter color, had different phys. and chem. properties and showed different therapeutic effects from the original oils. The oils evidently underwent deterpenation, which indicates that steam distn. might be a valuable means of studying the chemistry of such oils. The following data for the 5 plants in the order above give the consts. for the first distillate and for the steam-redistd. oil: d. 0.9161 ( $16^\circ$ ), 0.9129 ( $17^\circ$ ); 0.9497 ( $20^\circ$ ), 0.9451 ( $16^\circ$ ); 0.9412 ( $15.5^\circ$ ), 0.9206 ( $14.5^\circ$ ); 0.8824 ( $13^\circ$ ), 0.8784 ( $11^\circ$ ); 0.9314 ( $13^\circ$ ), 0.9385 ( $13^\circ$ );  $n_D^{20}$  23.33 ( $16^\circ$ ), 22.56 ( $17^\circ$ ); 22.76 ( $20^\circ$ ), 14.50 ( $16^\circ$ ); —, —; —32° ( $13^\circ$ ), —31.9° ( $11^\circ$ ); —, —1.6° ( $13^\circ$ );  $n_D^{1476}$  (16°), 1.475 ( $17^\circ$ ); 1.467 ( $20^\circ$ ), 1.470 ( $16^\circ$ ); 1.488 ( $15.5^\circ$ ), 1.475 ( $14.5^\circ$ ); 1.4778 ( $13^\circ$ ), 1.477 ( $11^\circ$ ); 1.5076 ( $13^\circ$ ), 1.503 ( $13^\circ$ ); soly. in 80% EtOH 1:8, 1:8; 1:1, 1:1; 1:20, 1:12; 1:12, 1:12; 1:2, 1:2; color yellow-green, light yellow-green; yellow, pale yellow; blue, blue; golden yellow, light golden; yellow-red, light yellow; odor camphor, camphor; camphor, camphor; pungent agreeable, pungent agreeable; pleasant, pleasant; amyl, amyl; taste bitter, bitter; bitter, bitter; bitter, bitter; bitter, bitter; burning, burning; acid no. 1.08, 2.20; 0.80, 0.97; 11.48, 12.04; 2.41, 3.92; 9.10, 10.57; sapon. no. 14.23, 18.45; 20.90, 22.54; 23.42, 27.24; 24.82, 29.62; 9.38, 11.85; ester no. 13.15, 16.25; 20.20, 21.57; 11.94, 15.20; 22.41, 25.70; 0.28, 1.23; % esters (bornyl acetate) 4.60, 5.69; 7.07, 7.55; 3.98, 5.32; 7.84, 8.99; 0.098, 0.45; sapon. no. after acetylation 49.69, 52.09; 69.00, 70.06; 47.45, 49.59; 56.31, 63.29; 159.33, 173.91; % free alcs. 10.28, 10.43; 13.45, 14.46; 10.24, 9.96; 9.95, 17.37; —, —; % combined alcs. 3.61, 4.47; 5.55, 5.87; 3.28, 4.18; 6.16, 7.06; —, —; 1 no. (max. per 0.1 g.) 248.3, —, —, —; —, —, —, —, —. The oils reacted with Br and I as follows: *Rosmarinus officinalis*.—Three drops of oil faded the color of 1 cc. of 5% Br in  $\text{CHCl}_3$ , 5 drops decolorized it, 3 drops changed a 5% I in petr.-ether from violet to wine-red and 1 drop gave a light red color with 1 cc. of alc. HCl or with concd.  $\text{H}_2\text{SO}_4$ . *Lavandula stoechas*.—Four drops of oil decolorized 1 cc. of 5% Br in  $\text{CHCl}_3$ , leaving a greenish nuance, 1 drop gave a red-brown ppt. and coloration of the supernatant liquid with 1 cc. of 5% I in petr.-ether, a light red with 1 cc. of alc. HCl and a blood-red with concd.  $\text{H}_2\text{SO}_4$ . *Thymus capitatus*.—Three drops changed the bright red color to yellow-red of 1 cc. of 5% Br in  $\text{CHCl}_3$  and the red-violet of 1 cc. of 5% I in petr.-ether to light red. One drop gave a wine-red with 1 cc. of alc. HCl and a red with concd.  $\text{H}_2\text{SO}_4$ . *Artemisia arborescens*.—One drop gave a brown turbidity with 1 cc. of 5% Br in  $\text{CHCl}_3$ , an intense brown with 1 cc. of 5% I in petr.-ether, no change in color with 1 cc. of alc. HCl and an intense red-brown with concd.  $\text{H}_2\text{SO}_4$ . *Teucrium polium*.—Three drops gave a blue with 1 cc. of 5% Br in  $\text{CHCl}_3$ , 1 drop changed the color of 1 cc. of 5% I in petr.-ether from red-violet to yellow turbidity and gave a yellow-red with 1 cc. of alc. HCl. Two drops in the last case gave a greenish brown color. One drop gave an intense red-brown with concd.  $\text{H}_2\text{SO}_4$ . The morphological characteristics of each plant are described. II. Essential oil of rosemary. *Ibid* 170-82.—The distn. products of rosemary were studied in greater detail. The expts. were carried out with plants from different localities and the results represent mean values. As with other essential oils (cf. Huerre, C. A. 14, 92) the I

no varied with the relative amts of oil and I, tests of the Sardinian rosemary oil and French and Sicilian oil all showing max. I nos at a definite excess of I. A detailed study of this point indicates that it is best to det. the I no. by making the measurements with increasing amts of alc I, using not over 0.1 g. of oil. In this way consistent results can be obtained and the max value, which will be with 0.9-1.0 g. of I, is accepted as the I no. Fractional distn. of the oil and analysis of the distillates showed only a trace of camphene, camphor in smaller amt. than in the Sicilian oil (cf. Pellini, *C. A.* 18, 146), about 17% cineole, which is also much less than in the Sicilian oil, and 13.89% borneol.

C. C. DAVIS

Determination of eugenol in oil of cloves; a simple titrimetric method for the quantitative determination of eugenol in ethereal oils. H. W. VAN URK. *Pharm. Weekblad* 62, 667-76(1925).—The method is based on the fact that the Na deriv. of eugenol is pptd quant from alk soln by satn. with NaBr. To 1 g. of oil in a glass-stoppered flask add 25 cc. 3% NaOH and shake. If the eugenol content is high the oil dissolves completely, otherwise the liquid becomes turbid. Add 22 g. NaBr, shake 5 min., then allow to stand 30 min. with occasional shaking. Filter through a dry 4.5-cm. filter and titrate 20 cc. of the filtrate with 0.5 or 0.2 N HCl and methyl orange. Toward the end of the titration a layer of Et<sub>2</sub>O is added to remove the turbidity of the non-phenols. Correcting for increase in vol due to addn. of NaBr and the soly of eugenol in the filtrate, the amt. of eugenol in mg. =  $(32/20) \times \text{cc. N acid} \times 164 + 40$ . A. W. DOX

Report on four years' experimental cultivation of peppermint in Western Australia. A. V. MARR. *Perfumery Essent Oil Rec.* 16, 181-2(1925).—It has been stated at various times that when peppermint is transplanted to districts outside its particular home in England, the chem and phys. properties undergo changes; also that the most important property, that of the aroma, is subject to alterations. The present report gives the results of several years' cultivation in western Australia and a comparison of the various analyses submitted, which have been taken over a fairly lengthy period, will show that the quality of the oil has shown comparatively little variation; from an analytical standpoint the constn. of true Mitcham peppermint oil have been well maintained. Furthermore, it developed that the menthol content became higher than in the Mitcham product, and considerably higher than that usually present in high-grade American peppermint oils.

W. O. E.

Citronellal content of oil of *Eucalyptus citriodora* (Hook). ALEXANDER ST. PFAU. *Perfumery Essent Oil Rec.* 16, 183(1925).—The findings by 4 quite different methods (Kleber's—titration with PhNHNH<sub>2</sub>—61.2 and 61.6%; Dupont and Labaune's—acetylation of the oximated oil—60.3 and 62.5%; Bennett's—titration with NH<sub>4</sub>OH—57.4 and 62.3%; Penfold's—bisulfite absorption in cassia flask—88 and 90% citronellal) are given, showing by 3 methods that the true citronellal content averages about 60%, and that the values around 90% are much too high.

W. O. E.

Evaluation of sublimate tablets. E. PERKS. *Pharm. Zentralhalle* 66, 369-70(1925).—For the speedy and approx. detn. of HgCl<sub>2</sub> in sublimate tablets the following volumetric procedure is suggested: Dissolve 2 tablets of 1 g. wt. or one 2 g. tablet in a graduated 100-cc flask and add distd H<sub>2</sub>O to the mark. Withdraw an aliquot of 10 cc of the liquid to a small round-bottom flask, add 2 cc. of 25% HNO<sub>3</sub> and 1 to 2 cc of starch soln., then run in slowly with continuous shaking 0.1 N KI soln. until a brown color (a mixed color due to the red ppt. and the blue of iodized starch) persists. The results compare favorably with those obtained by the Winkler method.

W. O. E.

Nicotine content of Philippine tobacco stems. W. L. BROOKS. *Philippine J. Sci.* 26, 497-9(1925).—The nicotine content of the tobacco stems secured from 5 different Manila cigar factories is given. Estimates are given which show that nicotine recovery at present prices would probably be a com. possibility, but under existing market conditions competition would result in an increase in price of stems. The growing of *Nicotiana rustica* for nicotine manuf. in the Isabela district would be unprofitable, but in places where cheap tobacco is now grown the growing of *N. rustica* for nicotine sulfate manuf. would be profitable.

W. O. E.

Semiselective antiseptic effect of the vapors of vegetable oils, their constituents and similar compounds. ORRO SCHÖNZ. *Philippine J. Sci.* 26, 501-4(1925).—Results of expts are given concerning the semiselective antiseptic effect of the volatile constituents of essential oils, vegetable oils, and similar volatile compds. toward *B. tuberculosis*, *B. typhosus*, *B. coli*, *B. dysenteriae*, *Vibrio cholerae*, *B. anthracis*, *B. pyocyaneus*, and Gram positive and negative pathogenic cocci.

W. O. E.

Method for the examination of neoarsphenamine and sulfarsphenamine. ELLAS ELVOYE. *U. S. Pub Health Repts.* 40, 1235-48(1925); cf. *C. A.* 18, 1877.—Dissolve

0.1 g. of the sample in 50 cc. of  $H_2O$  contained in a 200-cc. flask, add 50 cc. of 0.1 *N* I soln., mix, then add 10 cc. of 2*N* NaOH, rotate and allow to stand 5 min. at room temp. Now dil. with 21 cc. of *N* HCl and sufficient  $H_2O$  to fill to mark. Withdraw an aliquot of 50 cc. and titrate the free I with 0.1 *N*  $Na_2S_2O_3$ , using starch as indicator. Mix the remaining 150 cc. with 20 to 30 cc. of approx. 0.005 *M*  $Na_2AsO_3$ . When the color change indicates a completion of the reaction between the free I and the arsenite, transfer the soln. quant. to a 400-cc. beaker, add 5 cc. of *N* HCl, heat to boiling, treat with 5 cc. of 10% BaCl<sub>2</sub> soln., and det. the BaSO<sub>4</sub> in the usual way. The results are satisfactory and presented in tabulated form. Although I in alk. soln. readily oxidizes nearly all of the S of nearsphenamine to sulfate, it apparently does not act the same way on the organically combined S of sulfarsphenamine. Advantage is therefore taken of this difference in behavior between nearsphenamine and sulfarsphenamine for the purpose of differentiating between these 2 substances. Such treatment with I in alk. soln. apparently differentiates also between the organically combined methylene bisulfite and that which remains in the sulfarsphenamine as uncombined Na formaldehydebisulfite. In conjunction with other detns., such as the detn. of As, total S, quantity of sulfate before treatment with I, quantity of I required on direct titration, and quantity of I required in the presence of alkali, together with the deductions which may be made on the basis of these detns., it appears possible to evaluate, at least approx., the compn. of com. samples of nearsphenamine and sulfarsphenamine. The results obtained by using such a plan of analysis indicate that most of the samples of nearsphenamine examd. contd. but little sulfarsphenamine-like impurities. On the other hand, the results indicate that most of the samples did not contain enough organically combined S to account for a disubstitution product, and that in 2 of the preps. examd. there was not found sufficient organically combined S to account for even 50% of the monosubstitution product. In the samples of sulfarsphenamine examd., the results indicate that while some manufs. turn out a product which contains sufficient organically combined S to account for a 100% disubstitution product, 2 samples were encountered which apparently did not contain sufficient organically combined S to account for even about 50% of the monosubstitution product.

W. O. E.

The manufacture of arspenamine and its derivatives. W. W. MYDDLETON. *Chem. Age* (London) 12, 576-9(1925).—A review.

E. H.

The manufacture of vanillin from oil of cloves. J. McLANG. *Chem. Trade J.* 77, 3-4(1925).

E. H.

Mold spoilage in tobacco. C. H. LILLY. *Ind. Chemist* 1, 182-4(1925).—From a discussion of present-day practice of tobacco handling L. considers that treatment with AcOH as generally carried out is practically useless for preventing mold spoilage; but treatment with AcOH in presence of steam at about 80° would doubtless be quite effective.

A. PAPINEAU-COUTURE

Synthetic flavors. A. CHAPLET. *Parfumerie moderne* 18, 131, 133(1925).—Formulas previously published for artificial apricot, pineapple, banana, cherry, lemon, strawberry, raspberry, gooseberry, melon, orange, peach, pear, apple and plum flavors have been collected and tabulated.

A. PAPINEAU-COUTURE

Examination of some liquid petrolatum agar emulsions. L. E. WARREN. *J. Am. Med. Assoc.* 84, 1682-3(1925).—Numerous preps. are said to be emulsions of liquid petrolatum and agar. In addn. to these 2 constituents the preps. are reported to contain 1 or more of such substances as acacia, glycerol, phenolphthalein, sucrose, Na benzoate and sol. saccharin. The products analyzed were: Agarol Compound, Agrilin, Squibb's Liquid Petrolatum with agar, Petrolagar and Terraline with agar-agar. Qual. tests indicated the presence of agar and liquid petrolatum in each prepn., although the liquid petrolatum obtained from Terraline with agar-agar was highly colored and fluorescent. In addn. tests were made for each of the other substances which have been reported as present in the various preps. No product contained all of them. Substances precipitable by EtOH were present in all. Glycerol and Na benzoate were present in others. Sucrose was found in one (Petrolagar), phenolphthalein in one (Agarol) and saccharin in one (Terraline with agar-agar). Each of the products was of a white, or pale yellowish white color, except Terraline with agar agar which was pale lemon-yellow. Each was acid to moistened litmus paper. Each had a mildly sweet taste, except Agrilin, which was nearly tasteless, and Terraline with agar-agar, which was intensely sweet. Some of the preps. appeared to be flavored with vanilla. Analyses showed: liquid petrolatum and agar, resp.: Agarol 27, 0.6; Agrilin 33.2, 1.4; Petrolagar 61, 0.3; Squibb brand 44.7, 1.3; Terraline with agar-agar 39.8, 0.3%. The examn. reveals that the market preps. of liquid petrolatum with agar vary widely in their content of liquid petrolatum (27-61%) and considerably in their agar content. The largest

amt. of agar in any of the specimens examd. was equiv. to about 1.5% of agar U. S. P.  
L. E. WARREN

An aid in the biologic assay of cannabis preparations. BENJAMIN WHITE AND JOSEPH CIANCARULO. *J. Am. Pharm. Assoc.* 13, 813-4(1924).—To secure a sharper end point in detg. muscular incoordination in the U. S. P. assay of cannabis a dog was trained to walk on its hind legs when tempted by raw meat. After the administration of cannabis incoordination was considered established when the dog was unable to stand erect.  
L. E. WARREN

Cod-liver oil and its by-products. A. D. HOLMES. *J. Am. Pharm. Assoc.* 13, 1112-5(1924).—A brief essay giving the process of manuf., storage and uses of cod-liver oil and its by products.  
L. E. WARREN

Azo dyes from alkaloids of ipecac root and their identification by means of the spectroscope. S. PALKIN AND H. WALES. *J. Am. Chem. Soc.* 47, 2005-10(1925).—The method for the identification of phenols described in *C. A.* 18, 2303, has been extended to apply to certain alkaloids of ipecac. Azo dyes from these alkaloids of ipecac have been prepd. and measurements made of their absorption spectra in  $H_2O$ ,  $EtOH$  and  $Me_2CO$ . A no. of characteristic curves have been thus obtained for cephaeline and emetamine, the absorption spectrum max. of which can be used for their positive identification even in the presence of a considerable quantity of other drugs, if not unduly complicated by interfering substances. The absorption max. found are: cephaeline:  $H_2O$ , 5250;  $EtOH$ , 5550;  $Me_2CO$ , 6100. Emetamine:  $H_2O$ , 5700;  $EtOH$ , 5900;  $Me_2CO$ , 6275. The  $AmOH$ -sol. portion of the  $CHCl_3$ -insol. dye is used; the  $CHCl_3$ -sol. dye gives variable results.  
C. J. WEST

The perfume group (THOMS, *et al.*) 10. Synthesis of apomorphine (GADAMER, *et al.*) 10.

HÉGELBACHER, MARCEL: *La parfumerie et la savonnerie*. Origines, Recettes et formules, etc. Paris: Garnier frères. 212 pp. Fr. 7.50.

## 18—ACIDS, ALKALIES, SALTS AND SUNDRIES

FRED C. ZEISBERG

Observations on the manufacture of nitric acid by the synthesis of nitric oxide. O. SCARFA. *Ann. chim. applicata* 14, 368-78(1924).—In view of the growing importance of the electrochem. manuf. of  $NO$  (cf. Bianchini, *Giorn. chim. applicata* 1(1920); Hackspill, *L'Azote*, Paris, 1922; *C. A.* 16, 2583; Gros, *Rev. gen. electricité*, July 5, 1924) with condensation of  $N_2O_4$  to form  $HNO_3$  (cf. Guye, *C. A.* 17, 327, 1310; Raschig, *C. A.* 16, 2992) a study was made of the theoretical aspects to det. the most economic conditions. Since the dissociation const. of  $N_2$  and  $O_2$  are unknown, only 3 cases are considered, viz., where no dissociation occurs, where only  $O_2$  dissociates and where the same amts. of  $N_2$  and  $O_2$  dissociate. These correspond to the 3 reactions:  $N_2 + O_2 \rightarrow 2NO$ ,  $N_2 + 2O \rightarrow 2NO$  and  $N + O \rightarrow NO$ , and based on the work of Langmuir (*C. A.* 6, 3348) they comprise the technically important conditions. Calling  $A$  and  $B$  the % vols. of  $N$  and  $O$  introduced into the furnace,  $\gamma$  the % vol. of  $NO$  in the issuing gas and  $v$  the vol. of a g.-mol. of gas at the temp. and pressure in the furnace, it is shown that  $K_1 = \gamma^2 / \{ [A - (\gamma/2)] [B - (\gamma/2)] \}$ ;  $K_2 = [200 \gamma^2] / \{ [A(200 + \gamma)/(A + 2B) - \gamma] [B(200 + \gamma)/(A + 2B) - \gamma] \}$ ; and  $K_3 = [100 \gamma] / \{ [A(100 + \gamma)/(A + B) - \gamma] [B(100 + \gamma)/(A + B) - \gamma] \}$ . From these the yield of  $NO$  can be shown graphically as a function of the %  $O$  in the mixt. for the 3 conditions of dissociation. Since the actual yield varies with each type of furnace, the relative yields can be expressed by calling the yield of  $NO$  from air 1. In this case the yields are all a max. at about 50%  $O$  and are about 1.5, 1.3 and 1.2 for the 3 conditions of dissociation. Plotting the increase in the yield as a function of the %  $O$  added to the air, in which case the max. increase occurs with 57%  $O$  added to the air, the change in the yield is slight over a wide range in the %  $O$  added. In practice these calcs. are not strictly true, for a loss of  $O$  occurs, necessitating a replenishment. If  $p$  is the no. of m.<sup>3</sup> of gas lost per 100 m.<sup>3</sup> introduced,  $\gamma$  the no. of m.<sup>3</sup> of  $NO$  formed,  $x$  the wt. of  $NO$  per m.<sup>3</sup> and  $B$  the %  $O$  in the gas, then for each  $(0.46\gamma)/x$  kg. of  $N$  reacting,  $(pB)/100$  m.<sup>3</sup> of  $O$  is lost. Therefore  $(0.0214 \cdot pB)/\gamma$  m.<sup>3</sup> of  $O$  must be added per kg. of  $N$  reacting. A part of this is in the air supplied to compensate for the lost  $N$ , the remainder must be added as  $O$ . The latter is  $[0.027 \cdot p \cdot (B - 21)]/\gamma$  and since 1.37 m.<sup>3</sup> of  $O$  per kg. of  $N$  reacting is consumed (it is assumed that there is no loss), the total amt. of  $O$  consumed per kg. of  $N$  reacting is  $1.37 +$

$[0.036p(B - 21)]/\gamma$ . Graphs show the latter as a function of  $B$  when  $p$  is 0, 1, 2 and 4 for each of the 3 conditions. To calc. the most economical conditions for producing NO, the consumption both of O and of elec. energy must be included. If  $G$  is the energy absorbed per 100 m.<sup>3</sup> of gas introduced, the energy expended per kg. of N reacting is proportional to  $G/\gamma$ ,  $G$  being a function of  $B$ . On this basis graphs can be constructed to show the total cost per kg. of N reacting as a function of  $B$  for different values of  $p$ . This method proves that the most economical conditions correspond to a smaller value of  $B$  than those corresponding to the max. theoretical yield of NO. Assuming a 2% loss and no dissociation, the most economical conditions, i. e., the max. industrial yield, correspond to a mixt. of N and O contg 43% O. Owing to insufficient data on the process, these calcns. are only approx. Since O is a by-product of the manuf. of  $\text{CaCN}_2$ , an economical process for the manuf. of  $\text{HNO}_3$  from NO should be possible by utilizing the O of the  $\text{CaCN}_2$  process. Likewise a fertilizer contg both  $\text{CaCN}_2$  and nitrate might also be developed. Calcns. show that 25,000 tons per yr. of  $\text{CaCN}_2$  (contg 20% N) and 3800 tons of  $\text{HNO}_3$  (100%) could be produced with a consumption of 15,000 kw. C. C. D.

Solubility of a mixture of hydrogen and nitrogen in liquid ammonia. A. T. LARSEN AND C. A. BLACK. *Ind. Eng. Chem.* 17, 715-6 (1925).—Synthetic liquid  $\text{NH}_3$  carries with it appreciable quantities of dissolved N and H, rendering it undesirable for certain purposes, e. g., refrigeration. A mixt. of N and H (1:3) was passed through a wash bottle contg. anhyd.  $\text{NH}_3$ , samples of the liquid were withdrawn and analyzed for N and H. Tables and curves are given for temps. from  $-25^\circ$  to  $22^\circ$  and pressures of 50, 100 and 150 atm. A positive temp. coeff. is shown. W. C. EBAUGH

The production of ammonium bicarbonate and carbon dioxide at the Lepoldau works. H. KLIMBERG. *Z. österr. Ver. Gas u. Wasserfach.* 65, 93-6 (1925).—From gas water contg. 1.5%  $\text{NH}_3$  and 1.7%  $\text{CO}_2$  the latter is recovered in approx. 80% yield and 99.5% purity, it being then used to prep.  $\text{NH}_4\text{HCO}_3$ . Disclosure of the app. and operating conditions is carefully avoided. WM. B. PLUMMER

Calcium cyanamide, its importance in industry and in agriculture. MARCEL REMY. *La nature* 53, i, 218-22 (1925).—A description, including the chemistry of  $\text{CaCN}_2$ , its prepn., properties and uses. C. C. DAVIS

Heat economy in potassium chloride manufacture. O. KÖSTER. *Kali* 19, 127-30 (1925).—No new data are given. A general discussion is given of how to reduce the live-steam demands by using exhaust for heating purposes instead of condensing engines, by the use of preheaters, flash evapn., multiple-effect evaporators and suitable condensers and vacuum and air pumps. L. A. PRIDGON

The sulfur industry in Sicily. E. RICHTER. *Stenskt Pappers-Tid.* 27, 248-9 (1924).—Descriptive. W. SEGERBLOM

Production and properties of titanium oxide. R. H. MONE AND C. WHITEMORE. *Can. Chem. Met.* 9, 153-6 (1925). E. H.

Baurite, its industrial importance and its new applications. ALBERT HUTIN. *La nature* 53, i, 204-6 (1925).—Descriptive. C. C. DAVIS

The manufacture of casein for adhesives, cements and paints. C. H. BUTCHER. *Ind. Chemist* 1, 250-3 (1925). E. H.

Scientific basis of lime-burning practice. G. KEPPELER. *Z. angew. Chem.* 38, 397-405 (1925).—Theoretical considerations in lime burning are discussed. The yield of  $\text{CaO}$  should be 56% of the  $\text{CaCO}_3$  used. If instead of 56%, the yield is  $A\%$ , the quantity of unburned lime is  $(A - 56)100/44 = 2.28(A - 56)$ , and the quantity of completely decomposed lime is  $100 - [2.28(A - 56)100/A]$ . Since the sp. gr. of  $\text{CaO}$  = 3.08, and of  $\text{CaCO}_3$  = 2.72, the  $\text{CaO}$  should occupy only about 50% of the original vol. of the limestone, but it is very porous and the shrinkage in vol. amts. to only 10-12%.  $\text{CaO}$  really exists in 2 forms; amorphous, with sp. gr. 3.08 and cubically cryst. with sp. gr. 3.40 and refractive index 1.83. The first is stable at lower temps, changing into the second at 400-430°. A diagram is given by which all other constituents can be detd. from the  $\text{CO}_2$  content. This is assuming no excess of air and theoretical yields, whereas in practice the  $\text{CO}_2$  content of the gas is usually between 15% and 35%, with a gas vol. of 3-10 cu. m. per kg. of limestone burned at 900°. The decompn. tension of  $\text{CaCO}_3$  is plotted against temp. The temp. of the reaction can be considerably lowered by the addition of reducing materials such as coal or org. matter. They disturb the equil. by reducing the  $\text{CO}_2$  to  $\text{CO}$ .  $\text{H}_2\text{O}$  vapor accelerates the reaction. The nature of the limestone used is important, particularly if other carbonates are present which have a lower decompn. pressure than  $\text{CaCO}_3$ . Formerly the furnace lining was always basic in nature, but there is now a tendency to use acid lining. However, the acid material shows greater vol. change with change in temp. and is therefore more brittle. H. SROGRTZ

**Condensation of formaldehyde with phenols.** H. BARTHÉLÉMY, *Rev. prod. chim.* 28, 361-3(1925) —The first step is considered to be the formation of saligenin (I) ( $\text{PhOH} + \text{CH}_2\text{O} = \text{HOC}_6\text{H}_4\text{CH}_2\text{OH}$ ). Under the influence of heat and of a suitable catalyst (strong acid or alkali), two or more mols. of I condense, either alone or with some of the residual PhOH, with elimination of  $\text{H}_2\text{O}$ . The dehydration reaction continues with gradual increase in the size of the mol, until the colloidal stage is reached. At this point the formula of the colloidal particle can be represented by either  $[(\Sigma \text{C}_6\text{H}_4\text{OCH}_2)_n\text{H}]\text{OK}$  or  $[(\Sigma \text{C}_6\text{H}_4\text{OCH}_2)_n\text{H}]\text{Cl}$ , according to whether KOH or HCl was used as catalyzer. The essential properties of the condensation products are, therefore, determined by the presence of the OK or Cl ion, resp., so that there are but 2 classes of condensation products, having opposite elec. signs, and each of which in hydroalcoholic suspension is flocculated in 24-48 hrs. by addn. of the other. Addn. of 5% of KOH stabilizes, and addn. of strong acid causes flocculation of, suspensions of the formophenolic resins. Final hardening takes place by further dehydration at  $75^\circ$  or over; but above  $90-95^\circ$  it should be carried out in an autoclave, as otherwise the rapid elimination of the  $\text{H}_2\text{O}$  will give a soft, spongy, formless mass.

**Evaluation of bleaching earths.** R. DECKERT, *Seifensieder-Ztg.* 52, 388-9(1925) —Bleaching power and oil absorption are the two essential characteristics of an earth, but for comparative evaluation the following information should be added: type, brand, acidity, %  $\text{H}_2\text{O}$ , sp. gr., size of grain or surface, approx. age of the earth, price, chem. analysis. The acidity is detd. as follows: boil 5 g. earth 5 min. with 75 cc.  $\text{H}_2\text{O}$ ; cool, fill to the 100-cc. mark and titrate 10 cc. of the filtrate with 0.1N NaOH and phenolphthalein, multiply the no. of cc. used by 0.73 to obtain % HCl. P. ESCHER.

**The specific gravity and adsorptivity of active charcoals.** H. KRESSE, *Chem.-Ztg.* 48, 687-8(1924) —In the detn. of the d. of active C the liquid medium is adsorbed on the C so that the d. obtained is a function of the sp. vol. of the liquid, the activity of the C, and the ratio of wt liquid / wt C. On plotting the detd. d. vs. the latter ratio, using the same C with different liquid mediums, curves are obtained which are concave upwards and which, while considerably different at low values of the ratio, all become asymptotic to the same horizontal line (the true d.). A ratio of 50 g. liquid / 1 g. C is recommended for d. detns. A general discussion of the prepn. and properties of active C follows.

WM. B. PRUMPTA

The mechanism of the fixation of N as NaCN (GUERNSEY, SHERMAN) 2.

**Fortschritte in der anorganisch-chemischen Industrie an Hand der deutschen Reichspatente dargestellt.** Edited and published by Adolf Bräuer and J. D'Ans. 2nd vol. 1918-1923. Part I edited by Josef Reistotter, et al. Berlin: Julius Springer. 1200 pp. 96 G M.

FRITSCH, J. Colles et mastics d'après les procédés les plus récents. Paris: Girardot & cie. 342 pp. Fr. 16.50.

MARGIVAL, F. Colles, mastics, luts et ciments. 679 formules pour la préparation des produits, etc. 2nd ed. revised and enlarged. Paris. Desforges. 282 pp. Fr. 15.

**Alkali cyanides.** STOCKHOLMS SUPERFOSFAT FÄBRIKS A.-B. Swed. 58,696, May 13, 1925.  $\text{CaCN}_2$  is mixed with C (if it does not already contain enough of it) and with alkali carbonate and chloride or fluoride. The mixt. is heated to redness, the resulting mass is cooled and leached with water or a dil. soln. of alkali cyanide preferably in a counter-current app. and the soln. is evapd. Cf C. A. 19, 1470.

**Continuous production of cyanamide solution.** S. G. SELHAAR, Swed. 58,521, April 8, 1925.  $\text{CaCN}_2$  and the necessary amt. of water are introduced into a vessel in which the  $\text{CaCN}_2$  is brought in suspension with the water. The suspension is passed successively by means of pumps or injectors from one vessel into another under application of  $\text{CO}_2$ -contg. gases in such a way that a neutral or nearly neutral soln. is obtained in the last vessel.

## 20—CEMENT AND OTHER BUILDING MATERIALS

J. C. WITT

**Cement manufacture.** JAMES WAYSON. *Ind. Chemist* 1, 231-4(1925) —A review. E. H.

**Influence of manganese content on hydraulic properties of blast-furnace slag.** RICHARD GRUEN. *Stahl u. Eisen* 44, 1405-9(1924) —Higher Mn is regarded as harm-

ful, especially on the early strength of cement in which it is used as an addition to clinker. The MnO content was varied from 0.8 to 11% in natural slags, and from low to some 13%. A distinct lowering of strength is produced at about 5% MnO. The entire series shows the MnO dissolved in the slag without crystals. Up to 5% MnO there is well-defined melilite, which dissolves the Mn. At 10% MnO the excess forms aggregations of dendrites between the clear idiomorphic rectangular melilite crystals. Dendrites appear green by incident light. The effect of Mn on pure fused mixts. was studied:  $3\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  disintegrates with Mn present, aluminates are almost unaffected by Mn; silicates lose what little hydraulic (secondary) properties they have. A. H.

The use of fluosilicates for hardening and rendering impermeable limestones and cements. J. LAZANNEC *La nature* 53, 4, 154-5(1925).—A general description of the chemistry and technical aspects. C. C. DAVIS

Open-tank creosoting plants for treating chestnut poles. T. C. SMITH. *Bell System Tech. J.* 4, 159(1925). C. G. F.

### Strength and related properties of wood (ANON) 2.

Compact, solid, indifferent bodies from hydraulic cements. J. U. A. OHLSEN. Danish 34,230, Feb 23, 1925. Datomaceous earth previously impregnated is mixed to a mortar with Sorel cement and molded under pressure, forming a non-porous material.

Production of oil and burned lime. G. H. HULTMAN. Swed. 58,571, April 22, 1925. Limestone is burned with bituminous alum slate in a lime kiln in discontinuous process, the oil being expelled at a lower temp., after which the kiln is ignited for lime burning.

## 21—FUELS, GAS, TAR AND COKE

A. C. FIELDNER

Important fuel developments during 1924. H. W. BROOKS. *Gas Age-Record* 55, 265-7(1925). H. G. BERGER

Calculation of the heating value of a fuel from its ultimate analysis. R. VONDRÁČEK. *Monat. Rundschau* 17, 317-21(1925).—The usual form of the Dulong formula  $Q = 81C + 290[H - (O/8)] + 25S$ , where  $Q$  is the (higher) heat of combustion and the letters represent the % of the resp. element in the fuel, is revised with the introduction of a variable coeff. for C, viz,  $Q = (89.1 - 0.062C')C + 270[H - (O/10)] + 25S$ , where  $C'$  is the % C in the pure combustible, i. e., is C cor. for the ash,  $\text{H}_2\text{O}$  and S contents. This formula, unlike the usual one, holds over the C range 45-90%. The % error in the heat of combustion calcd. for various C contg. substances is as follows, for the new and old expressions, resp.: Bituminous coal, -1.0 to +0.3, -2.2 to +0.9; brown coal, -2.0 to +0.3, 0 to -6.9; peat, +0.7, -7.2, wood, -0.3, -11.8; cresol, +0.1, +0.8; cellulose, -0.3, -13.6, crude oil, -0.5, +5.7. The (lower) heating value of the fuel may be obtained from either of the above expressions by addn. of the term -6(% moisture). WM. B. PLUMMER

Fuel application—the essential factor in furnace design. E. J. EVANS. *Iron and Steel Eng.* 2, 263-7(1925).—Rapid combustion causes more effective heating, a higher temp. of reaction, and a greater effectiveness of the radiant heat. Radiant heat is proportional to the fourth power of the abs. temp. It is the most effective form and by proper direction and reflection may be coned. or diffused after the manner of light waves. The combustion zone must be designed to favor rapid combustion. The entering mixt. should be at a high temp. and the mixt. must be baffled or its velocity retarded to the point where combustion is completed within the zone. Operating characteristics, arrangement of the burners and the size and shape of the combustion chamber are discussed. W. H. BOYNTON

Reducing excessive boiler fuel in small gas plants. C. L. C. KAH. *Gas Age-Record* 55, 39-40(1925).—General discussion of factors affecting the efficiencies of boilers in small gas plants. H. G. BERGER

The combustion of carbon. I. H. F. SMITH AND W. C. ERAUGH. *Ind. Eng. Chem.* 17, 694-5(1925).—A small exptl. producer, using charcoal as fuel, was connected with a second producer and a source of air in such a fashion as to permit either (a) burned producer gas, rich in  $\text{CO}_2$  and very hot, or (b) air only, to pass through the incandescent C in the exptl. producer. Thus a real sepn. of the so-called oxidizing and reducing zones could be effected. It was shown that the production of CO from  $\text{CO}_2$

in (a) was relatively small, whereas in (b) the CO content became large. Analyses of gases taken at various depths above the grate are shown in tables and graphs, and indicate that the "oxidizing zone" of a fuel bed is very thin indeed, and that the principle—if not the primary—product of combustion in a fuel bed at bright red heat or above is CO rather than CO<sub>2</sub>. W. C. EBAUGH

The theory of washing coal in the wet way. R. A. HENRY. *Rev. universelle mines* [7] 6, 246-78 (1925).—Chiefly mathematical, the subjects including the detn. of the yield of a washing plant, the chief processes for washing coal, sedimentation by vertical agitation, the influence of the diam. of the grains on sedimentation, the d. of dry coal as a function of its ash and volatile, washing by ascending currents and the laws of motion of solid particles in such a current, the laws of motion of particles in a horizontal current of H<sub>2</sub>O and the theory of alluviation. C. C. DAVIS

Washing characteristics of coal from the thick Freeport bed, Pennsylvania. H. F. YANCY. *Carnegie Inst. Technology, Coal-Mining Investigations Bull.* 16, 1-42 (1924).—A report of washing tests made at, and on thick Freeport bed coal from, the Indianola mine (Pa.) of the Inland Collieries Co. The sp. gr. analysis of the coal at 1 in. ring size was as follows: <1.30, 58.2% of the dry coal, 3.8% ash, 1.30-1.40, 24.8, 10.9; 1.40-1.45, 8.3, 22.5; 1.45-1.50, 2.1, 28.4; 1.50-1.60; 2.1, 33.4; 1.60-1.70, 2.4, 41.8; >1.70, 4.1, 62.9, total ash 11.0%. At 0.375 in. ring size: 66.3, 3.5; 17.6, 12.1; 4.0, 21.3; 2.6, 23.6; 2.8, 35.2; 1.7, 42.8; 5.0, 63.1; total ash 11.0%. The app. used was an Elmore 3 compartment jig; the best operating conditions found were 75 r. p. m., 41.8 tons raw coal fed / hr., strokes in 1st, 2nd and 3rd compartments, resp., 2.33, 1.875 and 1.625 in.; the actual yield under these conditions was 82.0% at 7.8% ash. In these tests no attempt was made to sep. an intermediate product suitable for boiler fuel, although this procedure is advisable from an economic standpoint; when it is not done the 3rd compartment of the jig could be dispensed with. The low yield obtained in the test above is partly due to the lack of sludge-recovery equipment. The sp. gr. analyses of the 1- and 0.375-in. sizes show that if conditions permit crushing to 0.375 in. the reduction in ash should be approx. 1 unit (%) greater for a given yield. The value of the cleaned coal, assuming reduction of 2.5 units of ash at a yield of 90% is such as to leave a margin of \$0.45/ton raw coal to cover cleaning costs and profits. Complete data are given on 3 jigging tests and on a no. of sp. gr. analyses other than those cited above. W. M. B. FRUMER

New Zealand brown coals. Preliminary examination of a coal resin from Central Otago. L. H. JAMES. *J. Soc. Chem. Ind.* 44, 241-2T (1925).—Yellow-brown to smoke-gray, more or less spherical masses of a translucent resin were collected in large quantities from certain bands in the coal seams. The resin was easily sep'd. from an outer softer crust and from the adhering coal. The resin is hard, brittle, many pieces show concentric shell structure and the fracture is subconchoidal. Methods used in detg., and limiting values are given for the characters, mean values for which are: d., 1.0441; m. p., 160-165° (indefinite); moisture 0.59%; acid value 44.32; sapon no. 46.2; iodine no. 174.4; combustion analysis, C, 81.70%; H, 10.64%; O (diff.) 7.66%. No N nor S is present. The resin is a complex mixt. Results of expts. with EtOH, MeOH, benzene, light petroleum, CHCl<sub>3</sub>, AcOH, gave from 15.5 to 57.8% sol. M. p. of exts. varied from 60° to 120° (indefinite). Boiling with aq. KOH produced little effect; for 15 hrs. with 0.2N alc. KOH followed by filtration and acidification with HCl gave a ppt. equal to 46.3% of resin used. Compu. of the ppt. was C, 78.07%; H, 9-85%; O, 12.08% and mean acid value was 74.50. The ppt. decompd. on distn. at 20 mm. pressure. A comparative table gives const. and % sol. for this Coal Creek Resin and Kauri resin, the acid no. of Kauri is much the lower and I no. slightly higher; otherwise they are similar. This resin forms extremely tough and adhesive films after treatment with CHCl<sub>3</sub>, which suggests expts. as to its use for making varnishes. W. W. HODGE

Rate of combustion of coal dust particles. I. Size classification of finely powdered coal by air currents. C. M. BOUTON AND J. M. PRATT. *Carnegie Inst. Technology, Coal-Mining Investigations Bull.* 12, 42 pp (1924).—Characteristics of coal dust in mines and problems involved in sepg. coal-dust particles are outlined; air sepn. is considered preferable to settling in liquids. The requirements for an air-elutriation method and drawings and descriptions with relative advantages of 7 such methods are given. From previous work on the rates of settling of particles falling in a viscous fluid it is concluded that the irregularly shaped particles of powd. coal carried up by the air would be somewhat larger than called for by Stokes' law for perfectly spherical particles. Expts. with a down-blast type of elutriator proved unsatisfactory because many of the original coal particles were broken into smaller ones. A horizontal settling method was also tried and rejected. An up-blast type of elutriation app. gave the best results. Data were

obtained on wt of dust elutriated at flow of 0.75 to 2.25, and in one series to 4.50 cm. per sec.; microscopic size analysis in microns and % wt of the different sizes, 0-15 to 74-300 microns, wt of dust elutriated and left as residue, sepn of minus 200-mesh Pittsburgh coal dust into 4 sized fractions. The approx colloidal content was 4.1%; above colloidal to 13.2 microns, 38.0%; 13.2 to 23.2 microns, 22.0%; 23.2 to 74 microns, 35.9%. In a set of graphs plotting coal dust elutriated vs time a regular curve which approaches a max in about 1 hr. was obtained with 0.125 g. and air flow at 0.75 cm. per sec. In the larger vertical up-blast elutriator (vertical stack 5 in. diam., 3 to 4 ft. long) charges of 50 to 100 g could be treated, each charge requiring 10 to 20 hrs. in the air stream for clean sepn. Samples of powd. coal free from particles outside the selected range gave the best results, 6 photomicrographs of satisfactory samples of sizes: 0 to 74, 0 to 5; 0 to 8.5, 15 to 20; 20 to 30, and 30 to 74 microns are given. For rapid microscopic examn. dry samples were used, for more detailed examn. the powd. coal was dispersed in pure glycerol. Approx. 4% of the dust was lost through close-grained filter paper, but porous refractory alundum was found to be satisfactory as a filter to recover the fine dust from the air leaving the elutriator. W. W. HONOR

A microscopic study of pulverized coal. L. V. ANDREWS. *Mech. Eng.* 47, 429-32 (1925).—The insufficiency of data regarding fineness of material passing 200 mesh as obtained in the standard sieve tests is discussed. The characteristics of 5 general types of pulverizers are enumerated. The best way to visualize differences in the product from pulverizers is by microscopic examn. Details for the prepn. of powd. coal for microscopic examn. and photomicrographs of 18 finely ground samples are given. Screen tests, percentages through 200 and 100 mesh, and % moisture are given for most of the samples. Differences in the microscopic appearance of the samples are discussed. Classification of samples on basis of % through 200-mesh does not indicate the degree of fineness below 200 mesh by a wide margin. In sampling, across the discharge pipe the finest material was at the surface and coarsest at the center of the discharge pipe hence a sampling pipe extending across the discharge pipe has been recommended. The standard 100-mesh and 200-mesh % method of testing pulverized coal is not complete enough to show the actual pulverizing work done, it may be misleading in the comparison of two samples; the microscope should be consulted or a more elaborate screen test run when it is desired to know exactly what quality of pulverized coal is being delivered by the machine. W. W. HONOR

New methods for dewatering peat. KARL HOMOLEK. *Chem.-Ztg.* 49, 391-2 (1925).—Peat is ground to a broth in wet mills, covered with a non-miscible liquid like  $C_6H_6$  and its homologs, benzine or petroleum (crude or refined), and filtered on a suction filter. The layer of oil prevents air channels from forming, and thus a dry peat contg. 25-28% moisture can be obtained from one running 85% originally. Only about 0.5% of the petroleum remains in the peat. The main portion of petroleum is sepd from the water collected in the filter and used for succeeding operations. Finally it may be distd. to recover the waxy material dissolved by it from the peat (cf. *Ger.* 364,176). W. C. EBAUGH

Attaining high efficiency in industrial heating. K. HUFFELMANN. *Stahl u. Eisen* 44, 1489-91(1924).—To heat or melt efficiently one must heat in the shortest time, with least expenditure of work, with least wear. Fuel energy, mech. and human energy, and wear and depreciation are involved. Max. temp.-drop does not mean the highest efficiency; rather, max. heat transfer is to be aimed at. This latter depends on temp. difference, time and on turbulence of gases. Max. heat transfer is had when combustion takes place in the actual working chamber of the furnace and when the flame impinges sharply on the bath or on the steel (solid). This is not always feasible. To effect longer flame Bunsen ingeniously suggests returning part of the waste gases to dil the flame. A. HENGELMANN

The economics of gas production on the thermal basis. GEORGE EVETTS. *Engineering* 119, 815-8(1925). E. H.

Future gas supply—a challenge and an opportunity. W. M. RUSSELL. *Am. Inst. Chem. Eng.* (advance copy) June, 1925, 3-5.—Future development of the gas industry is predicted along the lines of reduced heating value, elimination of oil enrichment, and 2-stage single unit carbonization and gasification. WM. B. PLUMMER

Progress of the gas industry in England, 1925. A. C. BLACKALL. *Gas Age-Record* 55, 127(1925).—A review. H. G. BERGER

Gas combustion systems. H. F. REHFELDT. *Gas Age-Record* 55, 137-8(1925). H. G. BERGER

Recent developments in the European gas plants. C. H. S. TUPHOLME. *Gas Age-Record* 55, 189-90(1925).—In cold weather live steam passed into the purification

boxes through the air line for reinvigoration increases the amt. of total  $H_2S$  removed. Tables show the data. The effect of temp. on outputs shows the fallacy of striving for high distn. temps., for greater throughputs and high thermal yields. By-products have been overlooked. A new type of coke-screening device is described. H. G. BERGER

Recent developments in European gas plants. C. H. S. TUPHOLME. *Gas Age-Record* 55, 7-8 (1925).—Descriptions of carbonizing retort gas producers and coke ovens. H. G. BERGER

Aids for the solution of gas compression problems. L. G. JONES. *Gas Age-Record* 55, 37-8 (1925).—Four curves are given: (1) for the calcn. of adiabatic compression temps.; (2) isothermal compressions; (3) h. p. required to compress million cu. ft. (atm. pressure) to various discharge pressures in 1 hr.; (4) h. p. required to compress million cu. ft. per day from an initial pressure to given pressure. H. G. BERGER

Changing from water gas to mixed gas. E. L. SPANAGEL. *Gas Age-Record* 55, 371-2 (1925). H. G. BERGER

Gas production from heavy fuel oils by partial combustion. J. E. HACKFORD. *J. Soc. Chem. Ind.* 44, 299-305T (1925).—A bibliography of the oil-gas patent literature is given. A small generator is described in which the gas outlet from the combustion chamber is at the rear below the burner, so that the flame is forced to double back on itself. The gas produced is approx. 160 B. t. u./cu. ft. contg.  $CO$  4-6,  $CO$  11-14, unsatd. compds 4-6,  $H_2$  2-5,  $CH_4$  1-3%. With very heavy oil (sp. gr. 0.900 or greater) the gas make is 95-100 cu. ft./lb. oil, while for gas oil it runs up to 120 cu. ft./lb., the over-all thermal efficiencies being the same (80-90%) for all types of oil, although operation is more satisfactory with the heavier oils. The yield of lamp black is directly proportional to the d. of the oil, it having been as high as 10% with a heavy Mexican bunker oil. Com. installations ("Hakol" process) are notable for their compactness, a plant with a capacity of 50,000 cu. ft./hr. having a chamber 36 in. long by 18 in. internal diam., auxiliary app. occupying approx. 16 sq. ft. Wm. B. PLUMMER

The Wellman mechanical gas producer. ANON. *Engineering* 119, 37-40 (1925).—A well illustrated article on the mechanical gas producer of the Wellman Smith Owen Engineering Corporation, Ltd. (London). The rotating parts are the producer body and the ash pan, while the coal feed part (top) remains stationary. In large sizes 4000-4500 lbs. of bituminous coal are gasified per hr. Mechanical operation (including poking) is employed throughout. If intended to yield a hot, 150 B. t. u. gas for metallurgical purposes the gas should leave the producer at about 1200 deg. F., and the thickness of the green-coal zone should not exceed 8 in.; but if a "cold gas" (180 B. t. u.) is wanted the green coal should be about 12 in. thick and the gas should leave at 700° F. W. C. ERAUGH

Gas firing for vertical gas ovens. HANS SÄHLBERG. *Gas u. Wasserfach* 68, 370-1 (1925).—Coke is replaced by oven gas in the ratio of 1.2 cu. m. gas per kg. coke. The advantages of the process depend on the relation between coal cost and coke selling price. Wm. B. PLUMMER

Relative value of carbon monoxide and hydrogen as constituents of producer gas for zinc distillation furnaces. Wm. E. RICE. *Bull. Am. Zinc Inst.* 8, No. 5, 120-34 (1925).—A brief summary of the work of several investigators on some phases of the problem of keeping the ratio of  $CO$  to  $H_2$  high. The use of producer gas in Hegeler and regenerative type furnaces has the following advantages: reduction of furnace coal consumption, reduction of labor, and increased life of clay retorts. Producer gas-firing insures ease of temp. regulation in large units and permits fuel saving by the recovery of waste heat in regenerative furnaces. In reviewing the reasons for the fact that gases high in  $CO$  make better heating mediums in furnaces than those of equal calorific value but low in  $CO$  and high in  $H_2$ , the factors discussed include: calorific values of gases, radiation from flames, flame temp., rate of propagation of flame and limits of inflammability, diln. by water vapor, and action of  $H_2$  flame on clay refractories. The advantage of  $CO$  over  $H_2$  is due to its higher net calorific value, the greater radiation from its flame, and its higher flame temp. The differences are shown in curves.  $H_2$  is undesirable in producer gas because of its short flame and the deleterious action of its surface combustion on furnace walls and retorts. The presence of a high proportion of  $H_2$  indicates diln. of the gas with undissociated water vapor. In Zn-distn. furnaces the production of high  $CO$  is effected by having the fuel surface exposed as large as possible, the time of contact between fuel and gas as high as possible and the temp. maintained as high as practicable. A min. quantity of steam to keep the fuel bed in proper condition is desirable. W. H. BOYNTON

The Chrisman downrun process. L. W. SELTZER. *Gas Age-Record* 53, 153-4 (1925).—All the gas made on the downrun is made to by-pass the carburetor and super-

beater because of the low temp. of the exiting gas. The carburetion is accomplished during the uprun only and as a consequence the rate of oil input is greatly increased over that of the usual practice. In this work, beehive-oven coke from the Pittsburgh district is used. A change in the cycle was found necessary whereby a longer run period was realized. A shortened blow realizes a saving in generator fuel of 2 to 3 lbs. per M. cu. ft. Tables are given to illustrate this H. G. BERGER

Recent tests on rubber joint rings for gas mains. WALTER HOLL. *Gas Age-Record* 55, 149-51 (1925); cf *C A* 18, 580.—The effects of solvent reagents found in coal gas were detd. on vulcanized rubber rings free and under compression. The tests consisted of vapor, immersion and impingement tests. The reagents used had no deleterious effect on properly vulcanized rubber of suitable compn. under the worst conditions. The absorption which took place was a phys. action. No absorption takes place when the rubber is prevented from distending or expanding. H. G. BERGER

Influence of incombustible constituents upon the practical utilization of illuminating gas. W. BERTELSMANN. *Gas u. Wasserfach* 67, 609-12 (1924).—Particulars are given of an investigation of the resp. efficiencies of utilization of various grades of mixts. of coal gas, water gas, and flue gases ranging in gross calorific value from 3547 to 6056 calories per l. when used in upright and inverted incandescence burners, in the boiling of water and in maintaining a furnace at a temp. of 1400°. The percentage of inert (CO<sub>2</sub> and N together) ranged from 12 to 30.8%. The results indicate that the effect of the inerts upon the relative thermal efficiencies of the resp. gases in use is so small as to be practically negligible. B. C. A.

The automobile truck using poor gas for use in the colonies. R. ANTHOINE AND E. WARNANT. *Rev. universelle mines* [7] 6, 126-43 (1925).—A discussion, with quant. data, of tests on trucks driven by poor gas from a gas producer using wood charcoal, including the amts. and compn. of the fuel and gases, the efficiency and the chem. and mech. engineering involved. C. C. DAVIS

Oil-gas plant at New Bedford. ROBERT LINDSAY AND L. M. PEASE. *Gas Age-Record* 55, 297-300 (1925). H. G. BERGER

Performance test of a scrubber-condenser. R. F. DAVIS AND J. H. ERWIN. *Gas Age-Record* 55, 405-6 (1925). H. G. BERGER

Brown-coal paraffin oil as wash oil for benzene recovery. FR. MÜLLER. *Gas u. Wasserfach* 68, 393 (1925).—No difficulty from thickening has been experienced at the Matbias Stinnes works (Karnap) in the use of a paraffin oil from brown-coal tar; the oil temp. must however be kept above 5° in winter. The small change in the oil observed in 6 mos. operation is shown by the following figures (resp. before and after): Engler viscosity at 50°, 1.40, 1.62; at 20°, 2.03, 2.82; sp. gr. 0.91, 0.93; % distd. at 200°, 4.0, 5.5; 300°, 20.0, 18.0; 300°, 76.0, 80.0; 400°, 98.0, 95.0. WM. B. PLUMMER

The presence of a sulfur compound in some grades of commercial benzene which contain no thiophene. E. PARISI. *Ann. chim. applicata* 15, 121-3 (1925).—In expts. on the peroxides of monoximes (C. A. 17, 2570; 18, 821) the presence of an unidentified compd., m. 124°, was reported. This has been proved to be diphenylsulfone, Ph<sub>2</sub>SO<sub>2</sub>, which was not formed during decompn. of the peroxide but was found as an impurity in the C<sub>6</sub>H<sub>6</sub> (Kahlbaum thiophene-free) used as solvent. Not all com. grades of C<sub>6</sub>H<sub>6</sub>, however, contain Ph<sub>2</sub>SO<sub>2</sub>. In analyzing the compd., the method of Dennstedt (*Anleitung zur vereinfachten Elementaranalyse*, Hamburg, 1919; cf *C A* 14, 609, *Ber* 38, 3729; 39, 1623; *C A* 3, 1381) for detg. C, H and S was found to be particularly rapid and accurate. The presence of Ph<sub>2</sub>SO<sub>2</sub> in some grades of C<sub>6</sub>H<sub>6</sub> contg. no thiophene is probably due to the method of removing thiophene, such as the use of concd. H<sub>2</sub>SO<sub>4</sub>, S<sub>2</sub>Cl<sub>2</sub>, Hg(OAc)<sub>2</sub>, etc. It is formed on distn. of PhSO<sub>2</sub>H, by oxidation of Ph<sub>2</sub>S and by the action of SO<sub>2</sub> or of PbSO<sub>4</sub>Cl on C<sub>6</sub>H<sub>6</sub>, and it is not improbable that these compds. are present in the reagents used for purification or may be formed at the time. C. C. D.

An early chapter in the benzene industry. W. IRWIN. *J. Soc. Chem. Ind.* 44, 92-4T (1925). E. J. C.

Lignite tars. IV. Basic constituents of lignite tar. F. FRANK AND P. VOLLMER. *Braunkohle* 23, 505-10 (1924).—The tar was treated with acids, and the bases were liberated from the acid soln. by the addn. of alkali and fractionally distd. The individual fractions were converted into their double salts with HgCl<sub>2</sub> and sepl. by fractional crystn. The fraction 160-170° gave β- and γ-picoline, α- and β-lutidine, and ε-codilline. The fraction 250-255°, after removal of aniline bases, yielded quinoline, isquinoline, a monomethylquinoline, 3 dimethylquinolines, and a trimethylquinoline. The higher fractions yielded quinoline, and the residue a monomethylquinoline which was isolated as its picrate. B. C. A.

Continuous tar distillation. G. ILBERT. *Asphalt u. Teerind.* *Ztg* 25, 394 (1925).—

In the continuous coal-tar distn. system of the firm of H. Hirzel, the tar is pumped from a reservoir to a preheater dehydrator (with superheated steam) to which is attached a condenser and separator for  $\text{NH}_3$  and raw benzene. The water-free hot tar is then introduced into a series of 2 to 6 stills arranged stepwise and heated by producer gas. Each still is connected with a sep. condenser. Steam is introduced into the last stills.

D. F. BROWN

The determination of paraffin in tars. C. PAROVANI AND I. UBALDINI *Ann. chim. applicata* 15, 17-32(1925).—There are various reasons why methods such as those of Holde (2 *angew. Chem.* 116(1897)) and Zaloziecki (*Dinglers polytech. J.* 274(1888)) are unsatisfactory even though in common use. A new method is described which differs in principle from the usual ones in that it seps. solid paraffins by virtue of the differing soly. of the paraffins and the residual tar in glacial HOAc (cf. *Ber.* 2, 2973(1888)). *Method*—Add to 3-4 g. of tar enough HOAc to dissolve it completely at the b. p., 70-80 cc. before heating and the rest slowly at the b. p., a total of 100-150 cc. usually being necessary. Cool to about 15°, the sepn. of paraffin being facilitated by rapid cooling and shaking. Let stand at 15°, filter, preferably by suction on a Pt cone (cf. Graefe, *Laboratoriumsbuch für die Braunkohlenteer Industrie* 71), wash with HOAc and then with 75% EtOH, also rinsing out all liquid, let the paraffin drain well, dissolve in hot petr.-ether (b. 60-75°) and collect in a separatory funnel in order to sep. the small quantity of dil EtOH, evap. in a weighed capsule, first on a steam bath and finally in a vacuum desiccator at 40-50°. The method is far easier and more rapid than that of Holde and Zaloziecki and gives the same results. Furthermore the paraffin is yellowish and odorless, is not greasy and has a higher m. p. than the blackish, odorous, resinous paraffin from the Holde or Zaloziecki method. Tests to det. the relation between the m. p. of paraffins and their soly. in glacial HOAc and the influence of temp. on this soly. show that the soly. at 15° increases slowly with increase in the m. p. and that the soly. increases rapidly with increase in temp. In these expts. the method of Pawlewski (cf. Stähler, *Handbuch Arbeitsmethoden Anorg. Chem.* 3, 1, 504) with slight modifications was found to be particularly serviceable. The method can be applied even to thick, dirty tars from the carbonization of peat, in connection with which quant. data show the results obtained with a peat tar distd. with direct heat, in superheated steam and after hydrogenation by the Bergius process. Hydrogenated tar contains less paraffin than before such treatment, probably because it is destroyed during hydrogenation. In detg. paraffin in pitch residues the latter should first be freed of coke and asphalt by dissolving in petr.-ether, filtering and evapp.

C. C. DAVIS

Conversion of cellulose, lignin and wood into humins by fungi (WEHMER) 11C. Structure of coals (MARCUSSEN) 10. The occurrence of crystalline paraffin in a Styrian brown coal (Dotchi) 8. Determination of N in coal, and coke (TER MEULEN) 7.

FISCHER, FRANZ: The Conversion of Coal into Oils. Authorized English Translation by R. Lessing. London. Ernest Benn, Ltd. 284 pp. 30s. net. Reviewed in *Ind. Chemist* 1, 258(1925). Cf. *C. A.* 19, 1622

SHURICK, A. T.: The Coal Industry. London. Harrap & Co. 403 pp. 10s. 6d.

Hard, coarse coke from peat and other inferior fuels. PATENTBOLAGET F. W. BRANDES & Co. Swed. 58,277, Feb. 18, 1925. The material is dried, impregnated and enriched in combustible matter by the gases from the coking furnace which are passed through it giving off the condensible components to the material. It is then introduced into the coking furnace, where the substances absorbed from the gas as well as part of the fuel itself will be decomposed into gas and substances high in C which will act as binders, making the material sinter together in a solid block of hard coke. The gas produced by the destructive distn. is passed through new amts. of raw fuel and the process repeated.

Apparatus for cooling coke. S. M. MIERKELSEN. Danish 34,305, March 23, 1925. A transportable atomizer placed on a track in front of the retort series.

## 22—PETROLEUM, LUBRICANTS, ASPHALT AND WOOD PRODUCTS

F. M. ROGERS

Percentage of gasoline increases. C. O. WILLSON. *Oil & Gas J.* 24, No. 2, 101-2 (1925).—The av. recovery of gasoline from crude oil in the U. S. during 1923 was 30.9%, in 1924 it was 33.1%, and for the first 3 months of 1925 it was 34.7%. D. F. B.

Larger units being installed for cracking gasoline this year. L. M. FANNING. *Oil & Gas J.* 24, No. 4, 82 (1925).—Ests. derived from a survey of cracking equipment in the U. S. predict an av. production of 225,000 bbl. of cracked gasoline per day for 1925. This would amount to 82,125,000 bbls for the year. It is estd. that 30,000,000 bbls of natural gasoline will be produced during the same period. D. F. B.

Modern treating methods in refining. G. W. REIM. *Oil & Gas J.* 24, No. 3, 119, 130, 132-3 (1925).—A discussion of acid and sweetening treatment. Costs of chemicals required for treatment are compared as follows: 13° Bé NaOH soln., \$0.0275; 20° Bé NaOH soln., \$0.048; 20° Bé. Doctor soln., \$0.06; NaClO soln., \$0.008; Ca(ClO)<sub>2</sub> soln., \$0.006; H<sub>2</sub>SO<sub>4</sub>, \$0.009. D. F. BROWN

The refining of petroleum in South Wales. JOHN CADMAN. *Petr. World* (London) 22, 265-71 (1925).—Analysis of the Persian crude oil used is given together with description of the methods used in refining under the headings primary distn., rerunning, hauxite treatment, SO<sub>2</sub> treatment, etc. D. F. BROWN

The cracking of mineral oils. J. LAZANNEC. *La nature* 53, i, 173-6 (1925).—A description of modern methods, with photographs and a flow chart. C. C. DAVIS

Distillation of petroleum oil in apparatus with a relatively large heating surface. D. WANDYEC, S. SUENAROWSKI AND CHMURA. *Przemysl Chem.* 8, 201-22 (1924).—The authors distd. residual oils remaining after the sepn. of gasoline and kerosene fractions from crude petroleum, using superheated gasoline vapor as heating medium. The app. comprised a boiler and superheater for the gasoline, a distn. column, a condensing column, a preheater for the oil, and a water-cooled condenser for the gasoline vapor. The capacity of the app. was 2.5 g. per hr. The gasoline vapor was brought to the required temp. in the superheater, passed successively through both columns, the condenser, and then back to the boiler, the circulation being continued until both columns had attained the required temps. The oil under treatment was then fed into the top of the distn. column, the residues flowing out of the bottom of the column, and the vapor passing through the condensing column. The more volatile constituents not condensed in this column were condensed together with the gasoline vapor in the water-cooled condenser, and at the end of the process were sepd. by distg. off the gasoline. The residues from the distn. column were passed repeatedly through the app., with gasoline vapor heated to successively higher temps., until only asphalt remained. The products were brighter in color than those obtained by the usual method of distn., showed violet to dark green fluorescence, were transparent in thin layers, quite odorless, had viscosity at 100° (Engler) up to 8.7, and could be easily refined. They compared favorably with those obtained from the same oils by distn. under high vacuum and by distn. with superheated steam. The vapor pressure of the heating medium must lie as near as possible to that of the most volatile constituents of the oil, and high-boiling gasoline fractions are consequently unsuitable for use as heating medium. B. C. A.

Fuel efficiency in plant operation. C. H. EDMONDS. *Oil & Gas J.* 24, No. 6, 130, 142 (1925).—It is calcd. that a 5000-bbl.-per-day refinery can afford to spend \$330,000 provided the fuel bill can be reduced one half. Similar calcs. are presented to show how the fuel bill may be reduced by increasing the furnace efficiency or the efficiency of heat exchangers. D. F. BROWN

Acid-treated and other clays used for refining petroleum products. E. C. BIERCKE. *Oil Age* 22, No. 6, 44-5 (1925).—It has long been standard practice to agitate the various kinds of vegetable oils with finely ground fuller's earth to decolorize the oil. The practice is now being adopted by petroleum oil refiners with marked success. In many cases gasoline can be refined in this way without the use of acid. In other cases the clay treat must be preceded by an acid treat. Kerosene requires a preliminary acid treat. It is predicted that the bulk of the clay used for this purpose in the future will be either raw clay or clay treated by some method other than digestion. D. F. BROWN

Insulation of cracking units with Tailor-Made blocks. H. B. WENTZ. *Nat. Petr. News* 17, No. 27, 77-9 (1925).—The type of insulation used on low-temp. stills is unsuitable on cracking app. because of the high temps. employed. A type of insulating block formed of diatomaceous earth mixed with South African blue asbestos and molded

into blocks which may be fitted around the surface of the still has been found to be more efficient. D. F. BROWN

Devises method for checking operation of natural-gasoline plants. P. TRUESDELL. *Nat. Petr. News* 17, No. 27, 63-9(1925).—A method for detg. the gasoline content of natural gas, etc., devised by R. B. Burr, comprises passing the gas through a specially designed charcoal absorber and then transferring the absorber to a special furnace, where the gasoline is expelled from the charcoal by superheated steam and passes to a condenser and fractionating column, from which stabilized gasoline is condensed. D. F. B.

General principles of charcoal testing. W. R. LENTZ. *Refiner & Nat. Gasoline Mfr.* 4, No. 6, 19-20(1923).—Description and app. for making field tests to det. the gasoline content of natural gas. D. F. BROWN

Hydrocarbon determination. G. WEISSENBERGER AND L. PIATTI. *Petroleum* 2, 21, 1145(1923).—A modified charcoal adsorption process is described. Adsorbed products are expelled by distg. with tetrahn. D. F. BROWN

Determination of water in petroleum fuel oil. L. SWETLOW. *Nefteyanoe i slancevoe Khozaystvo* 7, 533-7(1924).—S. examd. the method of von Lissenko, in which a sample diluted with paraffin oil or benzine is allowed to stand in a graduated vessel at 70°, and the vol. of water read off, the same method, but with addn. of CuCl<sub>2</sub>, drying on the water-bath; centrifuging in a graduated vessel; and the method of Hoffman and Marcussen (cf. Martens, "Das Materialprüfungswesen," 1912, 440). Only the last 2 methods are trustworthy, and centrifuging has the advantage of convenience and rapidity. In the examn. of masut a 25-cc. sample with 25 cc. of benzine and 0.3 g. of CaCl<sub>2</sub> is centrifuged for 5 min. at 900 r. p. m. in a 60-cc. vessel. B. C. A.

Salient characteristics of fuel oil. A. P. BJERREGAARD. *Refiner & Nat. Gasoline Mfr.* 4, No. 6, 11-4, 26-30(1923).—Fuel oils may be classified as (1) residues from distg. crudes, (2) gas oils, (3) blends of 1 and 2, (4) residues from pressure distn. processes, (5) blends of 4 and 1, (6) naturally occurring crude oils, and (7) oils of classes 1 and 6 which have been subjected to special heat treatment. The characteristics of each class are discussed briefly and the tests usually applied to fuel oils are described. The no. of tests for a given fuel oil should be as limited as possible so as to admit the greatest possible no. of oils and so widen the sources of supply without detriment to the useful qualities of the oils obtained. D. F. BROWN

Equilibrium vaporization of gasoline. R. STEVENSON AND H. J. STARK. *Ind. Eng. Chem.* 17, 679-85(1925).—A modified form of the freezing-point method for detg. the mol. wts. of gasoline fractions gave results consistent within 0.6%. Equil. vaporization consists in maintaining equil. between all the liquid and all the vapor throughout the process of vaporization. The characteristics of equil. vaporization are (1) the liquid vaporizes completely without evidence of chemical change, (2) the whole process is strictly reversible in the thermodynamic sense. The curves represent not only the course of equil. vaporization but also the course of equil. condensation. When the vapor has reached a mol. wt. equal to that of the liquid (109 for the sample used) the latter has just disappeared and the vapor is gasoline in the gaseous state. (3) The mol. wt. of the last droplet to evap. was 140. (4) The b. p. of the final liquid in equil. with gasoline vapor at a pressure of 760 mm. was 115°. This is the lowest temp. at which this gasoline can be vaporized at a pressure of 760 mm. of its vapor. This procedure vaporizes gasoline with min. input of heat and min. change of entropy. The temp. corresponding to the points at which these curves end is called the Deppé end point and is a definite function of the entire volatility of the gasoline. D. F. BROWN

Distillation of New Albany shale. A. W. HOMBERGER AND F. M. SHIPMAN. *Petr. Times* 13, 995-7(1925).—Expts. were carried out to compare 4 different methods of retorting on this shale. The methods used were (1) atm. pressure, (2) use of superheated steam, (3) use of reduced pressure, and (4) insertion of Cu in the vapor line, using atm. pressure. Conclusion: Use of superheated steam is best with respect to yields of oil and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. The reduced-pressure method produces the best quality of oil. Use of superheated steam gives a larger % of N and S because part of the original bitumen is carried over by the steam. The S and N are in the shale and also the oil, in combination with each other, and the % of each in the oil is dependent upon the conditions of retorting. The I nos. and consequently the true unsatn. are proportional to the sp. gr. of the crude oil. The loss to H<sub>2</sub>SO<sub>4</sub> is the sum of the unsaturates and the compds. sol. in the acid. Retorting for oil is best done by allowing slow heating and plenty of time in the retort. D. F. BROWN

Process is evolved to recover oil from bituminous sands. L. E. SMITH. *Nat. Petr. News* 17, No. 23, 31-3(1925).—The McClave process of treating oil sands consists in digesting the sand in a prepd. soln. made of a certain soil (not specified) and contg.

enough Na salts to make a complete sepn. of the oil from the sand grains. Digestion is carried out at about 200° F. and the pulp is then discharged through a flotation machine, where the oil is floated to the surface and the clean sand withdrawn from the bottom of the tank. The oil coming from the machine is refined by distn. in a special still. Test data indicate that 320 lbs. of oil could be recovered from a ton of sand as compared with 240 lbs. by retorting. Cost of obtaining oil by this process is estd. at 75 cents per bbl.

D. F. BROWN

Methods used for the dehydration of oil-field emulsions. D. B. DOW, Bur. Mines, Repts. Investigations No. 2688, 16 pp (1925); cf. C. A. 19, 2408.—The various methods which have been developed for dehydrating oil-field emulsions are discussed under the following headings: Settling processes, dehydration by heat, centrifugal dehydration, chem. treatment, Tret-O Lite process, elec. methods, filtration. D. F. B.

Specific heat-specific gravity-temperature relations of petroleum oils. W. R. ECKART, *Mech. Eng.* 47, 535-40 (1925).

E. H.

Boilovers of burning tanks. H. HALL, *Oil World* (Calif.) 17, No. 43, 1; *Nat. Petr. News*, 17, No. 23, 66-72 (1925).—Expts. carried out show that the following conditions must exist if a burning oil tank is to boil over: (1) water must be present; (2) the oil must contain a certain proportion of heavy ends which will carry heat down to the bottom considerably in advance of the burning surface; and (3) the tank must contain sufficient viscous material to cause the formation of foam when the water at the bottom boils.

D. F. BROWN

Separation of paraffin wax from masut. B. MAXOROV, *Neftjanoe slancevoe Chozjajstvo* 7, 352-61 (1924).—Attempts to sep. paraffins from masut by the use of chem. precipitants were not successful.

B. C. A.

The history of the refining of paraffin wax in Scotland. JAMES CROOKS, *Chemistry & Industry* 44, 599-602 (1925).

E. H.

Formation of sludge in transformer oils. B. TYCHENIN AND N. BUTKOV, *Neftjanoe slancevoe Chozjajstvo* 7, 341-9 (1924).—The sludge formed in transformer oils consists of salts of org. acids ( $C_{11}$  to  $C_{21}$ ), produced by oxidation of the oils. The oxidation is accelerated by the presence of certain metals, particularly Pb and Cu, Pb being the more active of the 2. Zn, Sn and Fe have no catalytic action in the oxidation. The rate of acid-formation in the presence of Pb increases rapidly with time, and is hardly perceptible in the first hr. Different varieties of oil exhibit very different properties as regards the formation of sludge, and the presence of less than 2% of resinous constituents has no deleterious effect. The formation of resins in oils refined by treatment with Fe proceeds more rapidly than in unrefined oils. To test transformer oils, 100 cc. of the oil are heated at 120°, in the presence of a piece of Cu gauze 70 by 15 mm., for 70 hrs., a current of O being passed in at the rate of 6-7 l. per hr. The oil is poured hot into a graduated cylinder, and the volume of the ppt. noted. The acidity and resin content of the oil are also detd.

B. C. A.

Tetraethyl lead. ALICE HAMILTON, PAUL REZNIKOFF AND GRACE M. BURNHAM, *J. Am. Med. Assoc.* 84, 1481-6 (1925).—The production of tetraethyl lead for com. purposes resulted in the poisoning of 60 to 70 men and 10 deaths in a period of 13 months ending Nov. 1, 1924. Since that date improvements in equipment have been made so that only 2 serious cases have thus far been reported in 1925. The mixing of the tetraethyl lead with gasoline constitutes a danger, the extent of which is as yet undetd. to employees of refineries and service stations. The use of gasoline to which tetraethyl lead has been added constitutes a probable risk, to garage workers and to the public, of chronic Pb poisoning because the combustion of tetraethyl lead gasoline results in the formation of  $PbCl_2$ ,  $PbBr_2$  and  $PbSO_4$ , which pass into the air with the exhaust gases.

L. W. RIGGS

Cylinder and engine lubrication. A. L. CLAYDEN, *J. Soc. Autom. Eng.* 17, 58-61 (1925); cf. C. A. 18, 3209.—Tests carried out with a steam cooling system on the engine of a 5-ton truck showed that chl. practically ceases when the jacket temp. reaches 210-220° F.

D. F. BROWN

Oxidation important in lubrication. T. S. SLIGH, JR., *Oil & Gas J.* 24, No. 2, 123, 135 (1925).—The oxidation test for lubricating oils indicates the resistance of mineral oils to oxidation, and that oils of low oxidation number are desirable for service where the stability of the oil is an important factor in the service performance. The test is made in a closed vessel under standard conditions of temp. and pressure and O atmosphere, and oxidation is continued for a definite period of time.

D. F. BROWN

The resin content of Swedish pine-tar. A. CAROSCELLI AND CASP. SCHNEIDER, *Z. angew. Chem.* 38, 470-2 (1925).—By resin content is meant the material in the form of colophony, contg. abietic acid. Cf. Marcusson and Picard, C. A. 15, 3386, for a report

of the constitution of pine-tar. The alkali sol. portion of pine tar contains resin, fatty acids, hydroxy acids and phenols, the alkali-insol. portion, aldehydes, ketones, alcs and hydrocarbons. By extg. the alkali-sol. part with soda soln. and treating the ext. with benzene, the hydroxy acids and a part of the polyhydric phenols are sepd. The residue, in acid mixt. yields soda insol. phenols by acetylation. Finally the resin and fatty acids are sepd. by esterification, according to the method of Twitchell. "Umea-tar" (a pale Swedish pine-tar) and a dark com. tar, resp., gave: Water-sol. acids (recorded as AcOH), 1.10, 2.88, unsaponifiable material: (a) volatile in steam, 8.66, —13.96, (b) non-volatile in steam, 32.07, —; sol in soda: (a) sol. in ether (recorded as acetate), 13.38, —; (b) insol. in ether, —, 10.00; acids: (a) insol. in benzene, 12.8, 8.9, (b) fatty acids (recorded as ethyl ester), 4.8, 4.2; (c) resin, 16.5, 2.5.

HARRIET W. GIBSON

Preparation of medicinal vaseline from technical vaseline and from "masut" containing paraffin wax (DEMCHENKO, VORONOV) 17. Measurement of viscosity, especially of lubricating oils (DALLWITZ-WEGNER) 1. Production of oil and burned lime (Swed. pat. 58,571) 20.

Separating paraffins from liquid hydrocarbons. AKTIEBOLAGET SEPARATOR-NOBEL Swed. 58,706, May 13, 1925. The mixt. is cooled until the paraffins will sep. in the solid state. Before, during or after the cooling the sp. gr. of the liquid is raised to slightly above that of the heaviest paraffin by addn. of heavier liquid hydrocarbons, after which the paraffins are sepd. completely by centrifugating.

## 23—CELLULOSE AND PAPER

CARLETON E. CURRAN

Is the solution of cellulose in ammoniacal copper oxide a peptization? EMIL BAUER *Kolloid-Z.* 36, 257-9(1925); cf. following abstract.—The soln. of cellulose in Schweitzer's reagent has been considered a chem. reaction in which 1 mol. of Cu unites with 1 mol. of  $C_6H_{10}O_5$  to form one mol. of sol. complex by Hess, Weltzien and Messmer. Thus infers that  $C_6H_{10}O_5$  is the correct formula for cellulose and that Schweitzer's reagent and cellulose form a true soln. (cf. *C. A.* 17, 208; 18, 1384). But the  $Cu(OH)_2 \cdot NH_3$ -cellulose soln. is colloidal. Therefore, the data from which these conclusions were drawn should be analyzed from another point of view: that is, that the soln. is a 2-phase system with the Cu divided between the two phases, water and cellulose. Let  $(Cu_c)$  be the concn. of Cu in the cellulose and  $(Cu_w)$  be the concn. of Cu in the aqueous phase. When A and A' are initial masses of Cu and B and B' initial masses of cellulose and  $(Cu_c)$  is the same for both cases,  $A - B(Cu_c) = A' - B'(Cu_c)$  (the mass of Cu adsorbed in the cellulose is measured by the optical rotation) and  $(Cu_w) = A - B(Cu_c)$ . When values for  $(Cu_w)$  are plotted against the corresponding values for  $(Cu_c)$ , the curve is a characteristic adsorption curve represented by the formula  $(Cu_c) = \alpha(Cu_w)^{1/n}$ . In the case of cellulose in Schweitzer's soln.,  $1/n = 0.275$  and  $\alpha = 1.42 \cdot 10^{-3}$ . If  $x/m$  represents the mass of Cu adsorbed on 1 g. of cellulose,  $x/m = 1.42 \cdot 10^{-3} (Cu_w)^{1/3.64}$ . When the concns. are substituted in the equation representing the mass law no const. is found. The dissolving of cellulose in Schweitzer's reagent is a peptization.

F. E. BROWN

The solution of cellulose in ammoniacal copper solution. KURT HESS AND ERNST MESSMER. *Kolloid-Z.* 36, 260-4(1925); cf. *C. A.* 17, 208; 18, 1384.—In  $Cu(OH)_2 \cdot NH_3$  solns. typical cellulose-Cu salts as  $(C_6H_{10}O_5Cu)_2(Cu(NH_3)_4)_2$  are formed. At a certain concn. of NaOH the Cu-complex is decomposed and  $(C_6H_{10}O_5Cu)Na$  is formed. The optical rotation is a measure of the concn. of the complex cellulose-Cu ion. The reaction is represented by  $(C_6H_{10}O_5)_2Na + (Cu(NH_3)_4)(OH)_2 = (C_6H_{10}O_5Cu)Na + 4NH_3 + 2H_2O$ . The values found by expt. satisfy the equation  $(\alpha - \gamma k)^2 / [(b/x) - \gamma k] / \alpha k = K$ , in which  $\alpha$  is the total concn. of Cu;  $b/x$ , the total concn. of cellulose;  $k$ , a rotation value const., and  $K$  the const. of the equation. If one accepts Bauer's explanation (cf. preceding abstract) three important points must not be disregarded: (1) The action of Cu is specific. No other metal can replace it. The optically active complex forms according to chemical equivalents. (2) The reaction between Cu and cellulose results within wide limits independent of the degree of dispersion. In NaOH solns., easily sol., difficultly sol. and insol. cellulose result with the same sharpness as the mass law relation. (3) Cellulose may be replaced by truly dissolved carbohydrates as acetone glucose,  $C_6H_{12}O_6$ , and methylcellobioside,  $C_{12}H_{22}O_{11}$ . Tables of data and

graphs show that the agreement with the chem. equation is better than with the adsorption equation. F. E. BROWN

Reddening of sulfite cellulose. E. HÄGGLUND AND E. O. HEDMAN. *Svensk. Pappers-Tid* 28, 183-6(1925).—The intensity of the red color increases proportionately with the lignin content irrespective of the compn. of the digesting acid, if, before digesting, the wood is freed from components sol in  $\text{Et}_2\text{O}$ ,  $\text{Me}_2\text{CO}$  and  $\text{C}_6\text{H}_6$ . The red color is dependent on the lignosulfonic acid or its salts in the pulp. It may be diminished more or less completely by hydrolysis of the lignosulfonic acid although addn. of sulfite in itself does not cause the lignin to turn red, nor change the lignin mol. so that oxidation causes reddening. The acid nature of the sulfite digesting liquor probably causes this effect. Data of expts. substantiating these statements are cited. W. S.

Control in the pulp industry. R. DIECKMANN. *Papierfabr.* 23, Tech.-Wiss. Teil, 317-20, 333-6, 353-7(1925).—An address in which modern chem. control in the sulfite pulp industry is outlined. J. L. PARSONS

The determination of lignin in wood pulps. H. WENZL. *Papierfabr.* 23, Tech.-Wiss. Teil, 305-6(1925).—A discussion of the detn. of lignin by Schwalbe (*C. A.* 19, 2127). Since the analytical results by this method are lower than those by the more common methods, it must be assumed that the lignin complex has been attacked to a greater extent. J. L. PARSONS

The De-Vains process. WILLI SCHACHT. *Wochbl. Papierfabr.* 56, 550-5(1925); cf. *C. A.* 19, 1946.—A polemical discussion concerning the merits of the De-Vains Cl process for the manuf. of pulp. Straw, because of its fineness of structure, is not likely to replace wood in paper manuf. Straw production and utilization are discussed from an economical standpoint. J. L. PARSONS

De-Vains straw pulp. W. HERZBERG. *Wochbl. Papierfabr.* 56, 555(1925).—The approx. compn. of the paper used for the London "Morning Post" of Mar. 18, presumably composed of straw pulp manufactured by the De-Vains process, is groundwood 50, straw pulp 35, and chem. wood pulp 15%. J. L. PARSONS

The manufacture of pulp and paper from wood. ARTHUR KLEIN. *Zellstoff u. Papier* 5, 163-6(1925).—Summary of an address covering the mech. and chem. disintegration of wood, the prepn. of sulfite cooking acid, acid recovery, bleaching, reddening of pulp and the alk. digestion process. J. L. PARSONS

Experimental paper-making. W. Y. CROW AND Y. T. SING. *J. China Soc. Chem. Ind.* 3, No. 1, 113-26(1925).—Data are given on 6 small-scale expts. with Chinese raw materials, including rush, rice, kao-liang, bamboo. W. H. ADOLPH

Frothing and pin holes in coated papers. A. VERRILL AND E. SUTERMEISTER. *Paper Ind.* 7, 393-6(1925).—A discussion of the properties of froth, the more common causes of foaming and the use of foam reducers. A. PAPINEAU-COUTURE

The waste problem at news print mills. V. P. EDWARDS. *Paper Trade J.* 80, No. 24, 58-60(1925); *Paper Mill* 49, No. 23, 16, 18, 55-6(1925); *Paper Ind.* 7, 451-5(1925).—A discussion of the necessity and advisability of solving the waste sulfite liquor disposal problem and the problem of fiber recovery in pulp and paper mills. A. PAPINEAU-COUTURE

Pulp yields from spruce and balsam. G. J. ARMERUSTER. *Paper Trade J.* 80, No. 24, 61(1925); *Paper Mill* 49, No. 23, 22, 46(1925).—In com. operations rossed black spruce from Northern Ontario gave a yield of 1324 lbs. of unbleached sulfite per cord; a mixt. of 60% white spruce and 40% balsam fir from the Prov. of Quebec south of the St. Lawrence River gave 1111 lbs. per cord; and sap-peeled balsam fir from the same locality gave only 1010 lbs. per cord. The economic importance of these yields is discussed. A. PAPINEAU-COUTURE

Straw board and straw paper. H. G. FUNSETT. *Paper Trade J.* 80, No. 23, 58-60(1925); *Paper Mill* 49, No. 23, 30-4, 42(1925); *Paper Ind.* 7, 419-23(1925).—A description of it. process of manuf. A. PAPINEAU-COUTURE

Concentration of spent sulfuric acid from parchmentizing plants. M. SERVE-BRIQUET. *Pulp Paper Mag. Can.* 23, 695-6(1925).—See *C. A.* 19, 1946. A. PAPINEAU-COUTURE

Titration of sulfate pulp liquors. L. GUNDEL. *Papierfabr.* 23, Tech.-Wiss. Teil, 277-9(1925).—Expts. on a soln. contg. known amts. of  $\text{NaOH}$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_2\text{S}$ ,  $\text{Na}_2\text{SiO}_3$ ,  $\text{Na}_2\text{SO}_3$ ,  $\text{Na}_2\text{S}_2\text{O}_3$  and  $\text{Na}_2\text{SO}_4$  demonstrate that the total alkali in sulfate pulp liquor can be correctly detd. by titration with  $\text{I-NHCl}$ , with Me orange as an indicator. The effective alkali can be detd. by a similar titration after adding  $\text{BaCl}_2$  and filtration. The I-consuming constituents a<sup>n</sup> continually changing in compn.; after 2 days the I titer decreased about 2%, and after a month comparative figures could not be obtained. J. L. PARSONS

Behavior of calcium and magnesium bisulfite liquors on heating under pressure. C. G. SCHWABE and KURT BERNDT. *Wochbl. Papierfabr.* 56, 675-6(1925).—A reply to Weitzl (*C. A.* 19, 2131). The Mg bisulfite-sulfite equil., compared with that of the corresponding Ca salts, shows a greater tendency to form  $Mg(HSO_3)_2$ . The hydrolysis of  $MgCl_2$  solns., even at 25% concn., is practically nil when heated to 102-183°. It has not been shown that the hydrolysis occurs to a greater extent in the presence of fibers.

J. L. PARSONS

Review of recent domestic (German) and foreign patent literature concerning the utilization and development of waste liquors and gases in the pulp industry, 1912-1925. A. SCHROBE. *Papierfabr.* 23, Tech.-Wiss. Teil, 30-3, 63-5, 89-92, 158-61, 251-3, 284-7, 293-6, 306-7(1925).—Brief abstracts of patents.

J. L. PARSONS

Acid vapors during concentration of black liquor. E. ÖMAN. *Svensk. Pappers-Tid.* 28, 5-7, 32-5(1925), *Papierfabr.* 23, Tech.-Wiss. Teil, 365-9.—The vapors arising during the concn. of waste liquors are often acidic although the liquor is moderately alk. Ö. assumes that the liquor contains  $AcONa$ ,  $H_2O$ ,  $NaOH$  and  $AcOH$ , each in the disso-

ciated and the undissociated state. From  $K_w = [H][OH]$  for water at different temps. and from  $[H][C_2H_3O_4]/[HC_2H_3O_4] = 1.8 \times 10^{-4}$ , Ö. calculates that there must be undissociated  $AcOH$  in the black liquor, and a larger amt. of the org. acids having smaller dissociation consts. The concn. of the acid in the vapor in relation to the concn. of the acid in the liquid depends on the dissociation const. Detn. of  $p_H$  for solns. of  $AcONa$  and  $AcONa + NaOH$  and for black liquors of known compn. bear out the above statements. The use of phenolphthalein, thymolphthalein and other indicators is discussed.

W. SEGERBLÖM

The fertilizer value of lime sludge from sulfate pulp manufacture. A. KLEIN. *Zellstoff u. Papier* 5, 170-1(1925).—It is advantageous to use lime sludge from the sulfate pulp mill as a fertilizer on land poor in Ca. The compn. of the dry material from 4 mills was  $CaCO_3$ , 69-90,  $Ca(OH)_2$ , 2-11,  $CaSO_4$ , 0.03-1.67,  $Ca_3S_2O_7$ , 0.76,  $NaOH$ , 0.13-0.70, and silicates, clay, sand, etc., amounting to 7.52-21.26%. The moisture content was 18-42%, and the sp. gr. 1.1-1.5.

J. L. PARSONS

Theory and practice of rosin sizing. RUDOLF LORENZ. *Wochbl. Papierfabr.* 56, 636-9(1925); cf *C. A.* 19, 2129.—A general discussion of the mass action of free rosin.

J. L. PARSONS

Ventilation of drying rooms in paper plants with recovery of heat. K. L. THUNHOLM. *Svensk Pappers-Tid.* 27, 426-8(1924).—When the temp. of the moist air leaving the paper is low (38°) the temp. of the heated fresh air can be relatively high (28°) without discomfort to the workers. When the temp. of the moist air is 45° the temp. of the fresh air must be 25°. Curves show that the loss of heat per kg. of evapd. water when the initial temp. of the fresh air is 6° falls with rise in temp. of the moist air, but that it rises when the initial temp. is 30°. The effect of the temp. of the paper runway is discussed. The relative increase in production obtained by a faster circulation of air depends on the temp. of the runway.

W. SEGERBLÖM

Artificial leather with special reference to its manufacture from nitrocellulose (JENKINS) 29. Manufacture and testing of glue and gelatin (BLASWEDER) 29.

ROBERTS, JOHN R. The Dyeing of Paper. Wilmington, Del.: H. I. du Pont de Nemours & Co., Inc. 102 pp.

SCHUBERT, MAX: Die Cellulosefabrikation. Praktisches Handbuch für Papier- und Cellulosetechniker, kaufmännische Direktoren, Werkführer, sowie zum Unterricht in Fachschulen. 4th ed. revised and rewritten by Ernst Altmann. Berlin: M. Krayn. 279 pp.

Utilizing the heat from cellulose boilers. H. O. V. BERGSTROEM. *Swed.* 58,302, Feb. 25, 1925. The steam from the boilers is gathered in a system of steam accumulators. Mech. features.

## 24—EXPLOSIVES AND EXPLOSIONS

CHARLES E. MUNROE.

Silver azide: an initiator of detonation. C. A. TAYLOR and WM. H. REINKENBACH, *Army Ordnance* 5, 824-5(1925).—The prepn. and phys. properties of  $AgN_3$  are described briefly and its detonating properties are studied. Detonators can be made with a

main charge of nitro substitution compd. and a priming charge of  $\text{AgN}_3$  that can compete with 11g fulminate- $\text{KClO}_4$  detonators and may be superior under some conditions of humidity and temp. R. H.

Method of eliminating danger of explosion due to static spark in gas-oxygen apparatus. W. B. LEWIS AND E. F. BORUM *J Am Med Assoc.* 84, 1417(1925).—A small insulated wire was run from the reducing valve on the tank to the metal part of the mixing chamber. All connections were soldered. A bare Cu wire running through the breathing tube made metal connection at each end. A moist cloth cover from the metal of the mask around the rubber face piece established connection with the patient's face. A small brass chain was run from the patient's arm to the metal of the table. An insulated wire was run from the table back to a point on the metal standard of the machine. A heavy moist cloth was extended from the machine to the floor. The anesthetist and all persons about the table should stand on a moist bath mat on a tiled floor, or if the floor is of wood the mats must be properly grounded. L. W. RIGGS

The explosibility of brown-coal dust. HANS STEINBRECHER *Braunkohle* 24, 232-40, 269-73(1925).—In all expts. where not otherwise stated the ignition was by means of an elec. spark. The difference between the various methods of ignition is shown by the following values for the lower explosive limit for the same dust; by spark, 740 g./cu. m.; by an open (wood) flame, 450, by ammonite initiating charge, 130. The relation between explosibility and particle size is shown by the variation of the lower explosive limit for various sizes from the same dust, on 5800 mesh/sq. cm., 1407 g./cu. m.; on 7000, 1050; on 9150, 740, on 11000, 508, through 11000, 370. For a given dust (through 11,000 mesh) the explosive limits were approx. 300 and 1500 g./cu. m., the max. explosive effect being at 600 g. The effect of the % volatile matter in the coal is pronounced; for various samples, all through 11,000 mesh, with % volatile decreasing from 60 to 48.6, the flame length decreased from 21 m. to 17 m., in another series which decreased from 59.4 to 35.6% volatile, the explosivity, as detd. by the millivolts developed by a thermocouple in the explosion chamber, decreased from 10.0 to 3.5. Prevention of explosion by addn. of mineral matter required raising the total % of inert matter (original ash + added stone dust) to 30% for spark ignition or 40% for ammonite initiation, but larger expts. show that mine explosions can be smothered by "barriers" consisting of piles of stone dust so arranged as to be thrown over the whole cross section of the drift by an explosive wave. The influence of combustible gas on dust explosions is considerable; by suspension of a small quantity of dust (less than the lower explosive limit) the lower ignition point of a  $\text{C}_2\text{H}_4$ -air mixt. was decreased from 5.8 to 2.8%  $\text{C}_2\text{H}_4$ . The reduction in the % volatile of the dust by the partial distn. and combustion of the explosion is approx. from 58 to 38%, in another case from 60 to 49%. The CO content of the gas after explosion ranges from 1.5 to 7.0%, it being uniformly true that the finer the dust the more CO is formed. Wm. B. PLUMMER

Gas poisoning following powder explosions. D. C. WALTON *U. S. Naval Med. Bull.* 22, 259-92(1925).—The compn. of modern explosives and of their products when detonated or when burned is reviewed. The symptomology and treatment of poisoning by CO and by nitric fumes are described at length. L. W. RIGGS

Gravimetric determination of trinitrophenol in a mixture of picric acid and trinitro-m-cresol. L. DESVERGNES. *Ann. chim. anal. chim. appl.* 7, 65-6(1925).—A mixt. of picric acid and 2,4,6-trinitro-m-cresol will form a clear soln. on heating with a 5% soln. of  $\text{Na}_2\text{CO}_3$  and the alk. soln. at 50° should be dark red (positive Kast reaction) and, when treated with a bromine-bromate soln. and acidified, should not absorb Br (*C. A.* 16, 2465). Such a mixt. may be dissolved in a satd. soln. of picric acid (contg. 9% of acid, obtained by dissolving 100 g. of pure dry trinitrophenol in 1 l. of 96% alc., leaving the soln. to stand for 3 days at 15° and rapidly filtering off the crystals formed), by heating under a reflux condenser and the trinitrophenol which crystallizes out on cooling can be dried and weighed. 390 cc. of satd. picric acid (of which the exact strength is known) is measured at 15° and added to 25 g. of the substance under examn. and soln. effected on a boiling water bath. After keeping for 5 days at 15° the picric acid crystals may be filtered off and weighed, or the total wt. of the trinitrophenol and trinitro-m-cresol may be detd. on the filtered soln. without waiting for the crystn. of the acid by evapg. 150 cc. of the soln. *in vacuo*. B. C. A.

Determination of picric acid in the presence of other nitro compounds. L. DESVERGNES. *Ann. chim. anal. chim. appl.* 97, 7-100(1925).—The drawbacks of the alkalimetric method for detg. picric acid in presence of non-phenolic nitro compds. are avoided by dissolving 1 g. of the dried, finely powd. material in 95% alc., making up the soln. to 100 cc. with alc., and then treating 25 cc. with 25 cc. of a soln. contg. 40 g. of KI and 10 g. of  $\text{KIO}_3$  per l., and titrating the mixt. with 0.05 N  $\text{Na}_2\text{S}_2\text{O}_3$  soln. The method does not

give quite such exact results with mixts. of di- and tri nitrophenols as with mixts. contg. nonphenolic substances which do not react with the iodide iodate soln. A gravimetric method may be used in the case of a mixt. of picric acid and  $\alpha$ -mononitronaphthalene. Twenty g. of the dry powd. material is extd. 5 times with  $\text{CCl}_4$ , the soln. is allowed to stand for 3 hrs., and the crystals deposited are filtered off, washed with  $\text{CCl}_4$ , dried and weighed. The liquid is evapd. and the residue is dried at  $50^\circ$  and weighed. A correction of 0.22 g. is made for the soly. of picric acid in  $\text{CCl}_4$ . B. C. A.

Shipping of substances which evolve O (MÜLLER) 13.

DIXON, WILLIAM HEFORTH: *The Match Industry*. London: Pitman & Sons. 160 pp. 3s

## 25—DYES AND TEXTILE CHEMISTRY

L. A. OLNEY

Contribution to the theory of dyeing. G. ROSSI AND A. BASINI, *Ann. chim. applicata* 15, 4-16 (1925).—Various reasons are given to show that the theory of salt formation, of soln. of the dye in the fiber or of a combination of the 2 theories are inadequate to explain the known facts of dyeing. If filter paper is partially immersed in a colloidal soln., e. g., a dye, the colloid either (1) diffuses uniformly through the part of the paper not immersed or (2) it diffuses for a short distance and then coagulates, the solvent alone diffusing beyond this region. This simple phenomenon offers a method for detg. whether a colloid is negative or positive according as its behavior is like (1) or (2). A similar phenomenon is involved in the action of dyes and fibers, for dyeing is not explained by the formation of a salt or by soln. of the dye in the fiber but by adsorption of the dye by the fiber. The fiber acts as a true coagulating agent like  $\text{Al}_2\text{O}_3$  and both coagulates and adsorbs the dye. Dyeing takes place when the affinity of the secondary valences of the fiber for those of the dye is greater than those of the dye for the secondary valences of the solvent. For this reason a dye adsorbed by a fiber from  $\text{H}_2\text{O}$  may be given up again in  $\text{EtOH}$ . If the affinity of the secondary valences of the dye and of the fiber is not the max. affinity, then dyeing can take place only with the aid of a mordant, which with the fiber acts as a substantive dye and gives an adsorption compd. of a different character from that of the original fiber. The mordanted fiber is characterized by a greater affinity of its secondary valences for those of the dye, so that the latter is adsorbed from its soln. Likewise the mordant may show similar effects by forming an adsorption compd. with the dye, the secondary valences of which have a greater affinity for those of the fiber than for those of the solvent. In any case an adsorption compd. between fiber, mordant and dye is formed. The evolution of heat during dyeing, used in the past in support of the theory of salt formation, represents the heat of adsorption and coagulation (cf. Rossi, C. A. 18, 3510). Assuming that the proposed adsorption theory is correct, the presence of an emulsoid stabilizer in a colloidal dye soln. should diminish the adsorption of dye by the fabric (cf. Briggs, C. A. 18, 1752) and furthermore the intensity of the color should vary with the concn. of the dye. Expts. with Congo red, methylene blue, Pontecau 2R and bleu lumière on cotton, wool and silk show that (1) the amt. of dye adsorbed by an immersed fiber contg. an emulsoid stabilizer, such as gelatin, is less than that adsorbed in its absence and (2) the amt. of dye combined with the fiber is not a fixed quantity as demanded by the salt theory but varies within certain limits directly with the concn. of dye in the bath. In support of the theory of heat evolution due to coagulation, a colloidal  $\text{As}_2\text{S}_3$  soln. in a thermostat was coagulated by adding  $\text{HCl}$ . By comparing the temp. change with that occurring when the expt. was repeated with  $\text{H}_2\text{O}$  instead of  $\text{As}_2\text{S}_3$  soln. it was shown that heat was evolved on coagulation of the  $\text{As}_2\text{S}_3$ . C. C. DAVIS

Interesting sources of natural dyestuffs. C. D. MELL, *Textile Colorist* 46, 244, 310-2, 443-6, 511-3, 630, 634, 655, 769 (1924); 47, 31, 102, 110-1, 159 (1925); cf. C. A. 18, 754.—Data are given on the sources of a wide variety of natural dyes.

Properties basis of classifying dyestuffs; their grouping in alignment with physical properties. H. S. BRUSV, *Textile Colorist* 46, 559-61 (1924); cf. following abstracts.—B. proposes a more thorough detailed study of the properties of dyestuffs, so that a better comparison and selection of dyes, both for use alone and in combinations, may be possible. This paper is an introduction to the following papers and outlines the objects, plan and advantages.

CHAS. E. MULLIN

The justification of the type-properties basic research on the current list of dye-stuffs. H. S. BUSBY. *Textile Colorist* 46, 639-40(1924).—A plea for a centralized cooperative lab. for research and study upon the type-properties of dyes. Cf. following abstracts CHAS. E. MULLIN

The place of measured dye properties in the general manufacturing problem. H. S. BUSBY. *Textile Colorist* 46, 695-8(1924); cf. following abstracts —The advantages to both manufacturer and consumer of definite standards of fastness to light and other agents, as well as other properties of dyes, are discussed. CHAS. E. MULLIN

Exact means to relative tabulation of various dye properties (now recognized, and newly defined); the evolution and technic of properties measurements. H. S. BUSBY. *Textile Colorist* 46, 765-8(1924); cf. preceding abstracts —The methods of measuring and tabulating hue, satn., brilliance and sheen are discussed. C. E. M.

Some of the properties to be measured on each dyestuff, and their significance. H. S. BUSBY. *Textile Colorist* 47, 19-21(1925); cf. following abstract —The coeffs. of tinting power, principal tone, and combination power; points of initial characteristic hue, max. color effectiveness, and max. efficiency; as well as the effective percentage range, and the characteristics which dominate the effect of dyes in combinations, are discussed. CHAS. E. MULLIN

Methods of procedure, apparatus, and a system of physical analysis of coloring materials operating on a semi-automatic recording basis. H. S. BUSBY. *Textile Colorist* 47, 153-6(1925) —The general procedure of standardization and comparison of samples are described. CHAS. E. MULLIN

Classification of the methods of dyeing wool. J. MERRITT MATTHEWS. *Color Trade J.* 14, 77-81, 141-5; 15, 7-9(1924).—A general discussion of the theory and practice of wool dyeing. CHAS. E. MULLIN

Dyeing of cotton knitgoods. J. MERRITT MATTHEWS. *Color Trade J.* 15, 125-8(1924).—The color requirements and bleaching are discussed. CHAS. E. MULLIN

Dyeing yarn for carpets. A. K. ROBERTSON. *Textile Colorist* 46, 706-9, 774-7(1924); 47, 99, 102(1925).—The fastness requirements and various dyeing methods are considered. CHAS. E. MULLIN

Features in modern silk dyeing. J. MERRITT MATTHEWS. *Color Trade J.* 14, 125-8, 189-92(1924).—General. CHAS. E. MULLIN

Features in modern silk dyeing and bleaching. EMILE CAGLIOSTRO. *Color Trade J.* 15, 23-6, 47-50, 84-7, 111-4, 157-61(1924).—A general discussion. C. E. M.

Dyeing of hosiery. M. N. CONKLIN. *Color Trade J.* 14, 84-8; 15, 17-9(1924).—A discussion of the aniline black, diazotized, and S colors on hosiery. C. E. MULLIN

Recent progress in the vat dyestuff industry. BARRINGTON DE PUYSTER. *Color Trade J.* 14, 88-92, 177-80(1924).—A discussion of some recent patents. C. E. M.

Color in relation to dyeing. J. MERRITT MATTHEWS. *Color Trade J.* 14, 4-6, 173-6; 15, 138-41(1924); cf. C. A. 18, 3276 —A discussion of the distinction between intensity and depth of shade, the effect of adding white to different colors, and the use of various app. to classify colors. An est. is made of the quantity of different spectrum components of any color by the spectrophotometer, the use of the phototintometer to det. the relative strength of color components, and the spectrum of dyed cloth. A comparison is made of spectrum and dyed colors, the difference in dyestuff and pigment colors, and the opacity of white. CHAS. E. MULLIN

Orange II. RAFAELE SANSONE. *Color Trade J.* 15, 130-1(1924).—The mfg. methods are discussed. CHAS. E. MULLIN

Coloring matter from dithymolisatin. CANDEA. *Bul. Soc. Chim. România* 6, 113(1924).—Oxidation of dithymolisatin in alk. solution results in loss of CO<sub>2</sub> from the mol. and formation of a red triarylmethane coloring matter. B. C. A.

The manufacture of Direct Black. J. H. PLATT. *Ind. Chemist* 1, 234-6(1925). E. H.

Preparation of mauveine and various bases. A. COBENZL. *Oesterr. Chem.-Zig.* 28, 25-8(1925); cf. C. A. 10, 276.—Mauveine is regarded as a regular safranin, formed from phenyl-*p*-phenylenediamine and 2 mols. of *o*-toluidine, and in confirmation, details are given of its technical prepn. by the oxidation of a mixt. of these substances and aniline; *as*-phenylmethyl-*p*-phenylenediamine gives a redder dye, *as*-phenyl-*p*-tolyl-*p*-phenylenediamine a bluer one. Gray dyes are formed by heating nitrosodimethyl- or -diethyl-aniline (or a mixt. of these) with *as*-dimethyl- or -diethyl-*p*-phenylenediamine, and by oxidizing nitrosodimethyl-aniline with aniline bases. Blue safranines are formed by oxidizing a mixt. of *as*-dimethyl-*p*-phenylenediamine and aniline or other bases; the former may be converted into other blue dyes either by fusion with *p*-phenylenediamine or diazotization and coupling with  $\beta$ -naphthol. Sulfonated dyes related to

Meldola's blue are made (1) by heating Na  $\beta$  naphthol 6 sulfonate with nitrosodimethyl- or -diethyl-aniline and AcOH; (2) by direct sulfonation of the dye. All are bluish gray, and the ethyl compd.,  $C_{20}H_{17}O_2N_2S$ , is regarded as possessing a novel structure of the naphthophenazine type. 6-Methylanilinoquinoline, a brown solid, has been prepd. from *as*-phenylmethyl-*p*-phenylenediamine B. C. A.

Process for purifying caustic soda from mercerizing baths by elimination of organic matter. JACQUES PANIZZON. *Bull. soc. ind. Mulhouse* 91, 174-7(1925).—Sealed Note 2203 of Sept. 6, 1912. The process consists essentially in dialysis through parchment paper. Report. HENRI SUNDER. *Ibid* 177-82.—S. discusses the practical value of the process and concludes that the increased cost of evapn. due to diln. of the recovered NaOH is more than compensated by the value of the latter. Ultra-filtration would probably be more satisfactory and more practical than dialysis. A similar process was patented under Fr. pat. 552,476, of June 2, 1922, by Pinct. A. P. C.

Puce and bister obtained with dinitronaphthalene. JULES BRANDT. *Bull. soc. ind. Mulhouse* 91, 169-70(1925).—Sealed Note No 1842 of June 5, 1908. Dark puce or bister is obtained directly on the fabric by printing with dinitronaphthalene (1,8- gave good results, 1,5- did not) in presence of NaOH and trithioformaldehyde; e. g., the fabric is prepd. with 8° Bé. glucose, printed with: 1,8-dinitronaphthalene 20, trithioformaldehyde paste 20, alk. thickener (consisting of British gum thickener 11, H<sub>2</sub>O 5, 40° NaOH 41), 60, steamed 10 min. with dry steam, rinsed, and washed. The colors stand up well in boiling soap soln. They can be shaded with indanthrene, algal, etc., dyes. Without trithioformaldehyde the colors are dull and streaky. Report. LOUIS LORBER. *Ibid* 170.—According to Ger. pat. 84,989 of May 28, 1893, similar results are obtained by addn. of 240 g. of crystd. Na<sub>2</sub>S per l. of color; but this cannot be used with Cu rolls, and B.'s process constitutes an interesting novelty. A. PAPINEAU-COUTURE

The silk industry—past, present and future. W. M. SCOTT. *Proc. Am. Assoc. Textile Chem. Colorists* 1925, 143-4; *Am. Dyestuff Rept.* 14, 399-400.—An address. L. W. RIGGS

Tests for identifying artificial silk. ANON. *Am. Dyestuff Rept.* 14, 404(1925).—The following tests are announced by the U. S. Bur. of Standards: "When small samples of artificial silk are treated with equal parts of concd. H<sub>2</sub>SO<sub>4</sub> and I, the following reactions take place: (1) viscose silk turns a dark blue color, (2) acetate silk, yellow, (3) nitrocellulose silk, violet, (4) cuprammonium silk, light blue, (5) gelatin silk, yellowish brown. With concd. H<sub>2</sub>SO<sub>4</sub> alone viscose silk turns a reddish brown color and cuprammonium silk a yellowish brown" L. W. RIGGS

The development of the primary treatment of flax and its importance. FR. TOBLER. *Chim. Promuisklenost* 3, 7-9(1925).—A review. H. BERNHARD

Internal mechanics of fibers considered in relation to general colloid theory and technical practice. S. A. SNOATER. *J. Soc. Dyers Colourists* 41, 207-16(1925).—"The object of this paper is to formulate a general theory of fiber elasticity, which will be of use in rendering comprehensible much of the complicated behavior of fibers in industry. The views put forward are founded on the recent work on the elastic properties of fibers and yarns" L. W. RIGGS

Manufacture of printed fabrics. GEO. RICE. *Color Trade J.* 16, 15-6, 56-7(1925).—General. CHAS. E. MULLIN

Why cotton cloth is bleached by common agents. WM. B. NANSON. *Textile Am.* 42, No 2, 15-6; No 3, 12-5(1924).—General. CHAS. E. MULLIN

Luster finishing upon linen piece goods. RAFFAELE SANSONE. *Textile Colorist* 46, 359-63, 428-30, 647-4(1924); 47, 28-31, 156-9(1925).—Finishing is discussed fully under inspecting and measuring, cropping or singeing, damping, widening and lengthening, producing brilliant glazed, satcen effects with calenders, mangles, and beetles, singeing, permanent finishing, crimping, lapping or rolling, and fixing relief design by glazing, embossing, watering, and other special processes, etc. CHAS. E. MULLIN

Molds in textiles. W. S. RICHARDSON. *Textile Colorist* 46, 771-3(1924); 47, 226-8(1925).—Infection on the various fibers and the methods of prevention are discussed. CHAS. E. MULLIN

Wool-scouring waste liquors—composition and disposal. F. P. VEITCH AND L. C. BENDREY. *Trans. Am. Inst. Chem. Eng. (advance copy)* June, 1925, 3-22.—A discussion of the chief methods of purification of the waste liquors and of the possible utilization of the wastes. Also in *Am. Dyestuff Rept.* 13, 449-55(1925). A. PAPINEAU-COUTURE

3<sup>1</sup>,3<sup>1</sup>,3<sup>1</sup>-Trimethylaurin (o cresaurin) and 3<sup>1</sup>,3<sup>1</sup>,3<sup>1</sup>-trimethyl-N<sup>1</sup>,N<sup>2</sup>,N<sup>3</sup>-triphenyl-*p*-rosaniline (triphenyl ros-o-toluidine (GOMBERG, ANDERSON) 10. Indigo-like dyes of the

naphthalene series (FRIEDLÄNDER) 10. Dyes derived from phenanthraquinone (SIRCAR, GUPTA) 10.

Dye. J. P. H. OERS. Danish 34,077, Jan. 26, 1925. (1) A basic aniline dye is made to combine chemically with Ca silicate or with double silicates of Ca and an alkali metal. (2) A basic aniline dye is stirred out in an aq. soln. of alkali silicate, alone or in mixt. with  $\text{Al}(\text{OH})_3$ ,  $\text{BaSO}_4$ ,  $\text{CaCO}_3$ , china clay, lithopone or titanium white, before or during the working of the mass in a Kollergang until homogeneity is reached and the dye-stuff has been chem. bound.

## 26—PAINTS, VARNISHES AND RESINS

A. H. SABIN

Progress in the paint and varnish industry. HANS WAGNER. *Farben-Ztg.* 30, 1941-4, 2008-10(1925); cf. *C. A.* 19, 2418 F. A. WERTZ

Spectrophotometric measurements of paint vehicles and pigments in the ultra-violet. G. F. A. STUTZ. *J. Franklin Inst.* 200, 87-102(1925). E. H.

Acute dermatitis among painters employed in an industrial plant. J. A. TURNER. *J. Ind. Hyg.* 7, 233-8(1925). E. H.

A viscometer for paints. HANS WOLFF AND W. A. COHN. *Farben-Ztg.* 30, 1805-6 (1925).—A modified viscometer (cf. *C. A.* 19, 4) consists of a paddle rotated in the paint by a falling wt. attached to a cord running over a drum on the upper end of the paddle axis. The time required for the wt. to fall a definite height gives a measure of the relative viscosities. The brushing qualities of a paint are not solely dependent on the viscosity, but on compn. and other properties. On gradual addn. of volatile thinners to paints, the viscosity fell rapidly at first, then remained practically const. over a certain range, and then fell rapidly on further addn. Paints made by thinning oil-pigment pastes showed a much lower viscosity than paints of the same compn. ground in ready mixed form; this is accounted for by the finer pigment particle obtained by grinding in the paste form, and is in accord with the fact that in colloidal dispersions, the greater the degree of dispersion, the lower the viscosity. F. A. WERTZ

Catalysis of the drying of linseed oil. HERMANN VOLLMANN. *Farben-Ztg.* 30, 1742-4(1925).—A criticism of the theory of catalysis advanced by Slansky (*C. A.* 19, 001). The drying time of linseed-oil pastes of varying pigment content spread on glass plates in definite thicknesses, are tabulated. The influence of oil-insol pigments on the drying of linseed oil is the resultant of various components which probably are additive in their action, not all of which are yet definitely known. It appears certain, however, that the influencing factors include transfer of O through molecularly or colloiddally dispersed catalysts; adsorption of suspensoids even of low degree of dispersion on the double linkages of the glycerides; the film thickness of the oil and the colloid phys. character of the pigment; light conditions, flocculation and peptization through molecularly dispersed substances. F. A. WERTZ

Preliminary comparison of results on coatings exposed to accelerated testing cabinets and on roof. H. A. GARDNER AND H. C. PARKS. Paint Manufs. Assoc. of U. S., *Circ.* No. 232, 248-57(1925).—Single coats of various clear and pigmented lacquers, paints, and varnishes on black iron panels were exposed on the roof, on an accelerating test wheel, and in an  $(\text{NH}_4)_2\text{CO}_3$  test cabinet; results of inspection after exposure of 7.5 weeks, 290 hrs., and 212 hrs., resp., are tabulated, and photomicrographs of the films given. Regardless of whether the accelerated test wheel will det. in a few days how a coating will wear on exterior exposure, it appears to be of great value in securing quick data as to the comparative aging of exptl. coatings. F. A. WERTZ

Ultramarine (blue). L. BOCK. *Farben-Ztg.* 30, 2139-41(1925).—A summary of the present methods of firing and grinding ultramarines. Illus. F. A. WERTZ

Oil-soluble colors. ADOLF DAHL. *Farben-Ztg.* 30, 2208-9(1925).—Criticism and comments on the paper of Kirchdorfer (*C. A.* 19, 2418). F. A. WERTZ

The practical use of driers in varnish manufacture. H. RASQUIN. *Farben-Ztg.* 30, 2206-8(1925).—The drying metals should always be used in optimum quantities. Pb and Mn do not give best results except in combination, whereas Co may be used alone. The pptd. resins of the metals are the most satisfactory because of their uniformity and soly. F. A. WERTZ

The production of linoleum cements. FELIX FRITZ. *Farben-Ztg.* 30, 1969-71 (1925).—A review of the compn. and method of mfg. linoleum cements. F. A. W.

Rosin production in Germany. HANS KATINSKY. *Farben-Ztg.* 30, 2082-3 (1925).—A brief description of the methods used in tapping the pine trees and in producing rosin and turpentine. F. A. WERTZ

Rosin production in lower Austria. A. REICHERT. *Oesterr. Chem.-Ztg.* 28, 87-8 (1925).—Special drip cups and new type of tree incisions sponsored by rosin-producing associations in the black-fir district are in use on about  $\frac{1}{2}$  of the available trees. This improved collection method has for the first time furnished a domestic source of "W. W." grade of rosin. Proper protection of young trees will probably double present production. F. A. WERTZ

Stearin pitch. K. WÖRTH. *Farben-Ztg.* 30, 1806-7 (1925).—A brief review of the fat-splitting process by the use of autoclaves, with  $H_2SO_4$  with Twitchell's reagent, and by fermentation; and of the distn. of the fatty acids and final recovery of the stearin pitch residues. The quantity of pitch produced varies with the I no. of the fatty acids from which it is obtained; tallow yields 1.5 to 2.5%; bone fats, 3%; fish oil, 8%. The pitch consists not only of unsaponifiable substances present in the original fats, but of polymerization and condensation products formed from the fatty acids through splitting off of  $CO_2$ . The latter constituents account for the I no. of 50 to 70 which differentiates stearin pitch from petroleum pitch, and probably accounts for the good drying qualities of japans made from the former. Chem. analysis is very difficult; the Cu and Fe content usually found in the ash can be traced to the corrosive action of the fatty acids on the distn. retorts; the I no. is the most important control detn., especially when the pitch is to be melted with S to produce insulating varnishes. F. A. WERTZ

Coal resin from Central Otago (JAMES) 21. Manufacture of casein for paints (BUTCHER) 18. Resin content of Swedish pine-tar (CAROSELLI, SCHNEIDER) 22. Resin acids (SUZUKI) 10. Determination of water in oils, varnishes, etc. (WOLFF) 7.

## 27—FATS, FATTY OILS, WAXES AND SOAPS

H. SCHERUBEL

Committee report on oil and fat analysis. E. IMMENDORFER. *Collegium* 1925, 135-41.—Phys. and chem. methods of examn. of oils and fats are reviewed and discussed. Methods of avoiding emulsions during extn. with petroleum ether after sapon. will be studied. I. D. CLARKE

Extraction of oils from seeds and from almonds by solvents. E. WEISS. *La nature* 53, i, 215-8 (1925).—An illustrated description of modern methods. C. C. D.

Chinese tea-seed oil. II. P. H. SHU. *J. China Soc. Chem. Ind.* 3, No 1, 193-208 (1925); cf. *C. A.* 19, 1634.—Analyses. The properties of tea-seed oil commend its use in soap. W. H. ADOLPH

Hydrogenation of fats. K. BUTKOVSKII. *Khim. Promyshlennost'* 3, 21-2 (1925).—Expts. carried out with linseed and sunflower oils in the lab. of the Russian Government plant "Salolin" in Nizhn-Novgorod show that linolic acid absorbs hydrogen practically not at all before linolenic acid present has been converted to linolic acid. The results disprove the opinion of Marcusson and Meyerheim (cf. *C. A.* 8, 2271). A diagram illustrates the changes of Hübl value and solidification point during hydrogenation of the oils mentioned, without and with admixt. of hardened fat (salolin). H. B.

Synthetic edible fats. K. BUTKOVSKII. *Khim. Promyshlennost'* 3, 91-2 (1925).—A review of the processes applied in Russia for the manuf. of hardened fats. H. B.

Preliminary testing of olein. C. SIEFEL. *Z. deut. Öl-Fett-Ind.* 45, 217-9 (1925).—For the recognition of "true oleins" for the textile industry S proposes the following const., the first 4 of which had already been proposed:

	Sapon. Olein	Distillate Olein
1. Acid no. not below	175	185-200
2. Sapon. no. not below	190	187-202
3. I no. not above	90	90
4. Titer	10-12°	10-12°
5. Mackey test	1 hour at about 100°	
6. Sp. gr. 20°	0.899-0.904	0.899-0.904
7. Flash point, open cup.	160-190°	
8. Viscosity, Engler	7	

Conclusions: (1) The above limits will segregate substitution products from true oleins, especially when the titer is considered. (2) The detn. of the inner I no. gives no additional information. (3) In doubtful cases it is recommended to make (a) a steam distn. at 220°, when coconut or palmkernel oil acids can be recognized in the distillate; (b) fractional crystns. at 25° and at 10° of the residual liquid acids from (a), which will show whether solid acids of higher titer are present. P. ESCHER

Determination of unsaponifiable matter in fish oils and wool fat. M. AUERBACH *Z. deut. Öl-Fett-Ind.* 45, 273-4 (1925).—Wool fat soaps are insol. in petr. ether. Wool fat is completely saponif. in 1 hr. with 0.5 N alc. KOH. Fahrion's method (C. A. 14, 2994) gives correct results with wool fat. P. ESCHER

Changes in the properties of aqueous sodium oleate solutions by addition of benzene and oleic acid. A. HARNE. *Z. deut. Öl-Fett-Ind.* 45, 245-8, 263-4, 274-6, 289-90, 308-10 (1925).—Pure Na oleate solns. were examd. in several series of expts for their viscosity, lathering ability, elec. cond., vapor tension and migration nos. in neutral, alk. and acid solns. with varying amts. of alkalis, acid (oleic) and benzene. Results: (1) The viscosities of Na oleate solns. increase to a max. with increasing amt. of benzene or oleic acid or both, while the lathering heights vary in the opposite direction; increasing amts. of benzene or oleic acid or both increase the size of the soap micelle; a considerable time elapses in many cases to reach final stability. (2) The cond. indicates changes in the soap micelle in kind or in arrangement; the end points also require considerable time. (3) The low vapor tensions found cannot be due to dissolved Na oleate, which is insol., nor to oleic acid freed by hydrolysis, but are probably due to the interaction of the soap micelle and the benzene mols. (4) Considerable amts. of Na ions migrate toward the anode. (5) A comparison of the migration nos. with the cond. measurements shows that increasing amts. of oleic acid increases the size of the micelle. P. ESCHER

Higher fatty acids and their anhydrides; determination of iodine number and its products of reaction; separation of solid unsaturated from liquid unsaturated acids; cerotic acid from peanut oil; rubber substitutes. D. HOLBE. *Z. deut. Öl-Fett-Ind.* 45, 303-5 (1925).—The easy decompn. of the fatty anhydrides of unsatd. acid is brought about by the absorption of O with the formation of lower fatty acids, ketones, H<sub>2</sub>O, etc. The satd. fatty anhydrides are considerably more stable toward both air and water vapor. Baked goods contg. a high % of oleic anhydride could hardly be distinguished by taste from normal goods. Margosches' method of I no. detn. fails with cholesterol and with wood oil. Godbole isolated traces of cerotic acid from peanut oil. Pitch from fatty acid distn. is suitable for rubber substitutes. P. ESCHER

Catalytic fat splitting. W. SCHRAUTH. *Z. deut. Öl-Fett-Ind.* 45, 805 (1925).—A résumé. 1,4-Chlorotetralinsulfonic acid may be crystd. from H<sub>2</sub>O with 2 mols. of H<sub>2</sub>O of crystn. and in that condition is a good catalyst for fat splitting, like the Twitchell reagent. When crystd. from benzene without any H<sub>2</sub>O of crystn. the compd. has no fat-splitting power. P. ESCHER

Studies of candelilla wax and other vegetable waxes. A. LEYS. *J. pharm. chim.* [8] 1, 417-24 (1925).—To avoid emulsions and effect sharp sepn. of biphasic liquid mixts., add to 10 g. wax in a warmed bulb (C. A. 7, 909) 25 cc. alc. KOH (45-50 g. KOH per l.) and 50 cc. C<sub>6</sub>H<sub>6</sub> and heat to boiling with reflux for 15 min. Pour off the liquid (A) into another bulb, leaving a brownish, viscous varnish (B) adhering to the walls. Add to A 2 g. powd. NH<sub>4</sub>Cl and continue boiling with reflux for 30 min. Add 50 cc. of warm H<sub>2</sub>O and warm slowly so as to effect a perfect sepn. of the 2 layers C and D. Draw off the lower layer (C), add a boiling soln. contg. 10 g. CuSO<sub>4</sub> and heat the mixt. until it boils. Cool and filter the pptd. Cu salts of org. acids, wash with cold H<sub>2</sub>O and dry. Heating the salts with C<sub>6</sub>H<sub>6</sub> dissolves the Cu salts of the non-satd. acids. Hot treatment of the soln. with 20-30 cc. fuming HCl seps. Cu, leaving the pure unsatd. acid in C<sub>6</sub>H<sub>6</sub> soln. Similarly, the Cu salts of the satd. acids insol. in C<sub>6</sub>H<sub>6</sub> are decomposed by boiling with HCl in presence of C<sub>6</sub>H<sub>6</sub>; obtain the pure acid by evap. the C<sub>6</sub>H<sub>6</sub> solns. Put layer D contg. hydrocarbons, higher alcs. and the K salts of hydroxy acids into an oven at 110° for 24 hrs. to remove all traces of C<sub>6</sub>H<sub>6</sub>, then dissolve in boiling AmOH, heat to boiling with fuming HCl and cool. A cryst. mixt. of higher alcs. and acids beneath a cake of hydrocarbons results. The sepn. and purification of all these and of A are described. A com. sample of candelilla wax showed d<sub>4</sub> 0.991, m. p. 71°, acid no. 19.4, ester no. 34.1, ratio ester: acid nos. 1.75; I no. 12.9, H<sub>2</sub>O and volatile matter 0.52%, ash 0.75%. Ash-free wax gave hydrocarbons 54.3%, m. p. 66°, dropping point (app. of Ubbelohde, cf. C. A. 8, 2630) 63°, I no. 6.25, higher alcs. and "special acids" 41.0, satd. acids 4.2% of m. p. 69°. S. WALDBOTT

The analytical determination of hydrophenols (cyclohexanols) in soaps and their behavior toward chromic acid. K. LINDNER AND J. ZICKERMANN. *Z. deut. Öl-Fett-*

*Ind* 45, 189-90; 205-8(1925).—(1) Published detns. of hydrophenols in soaps do not agree with each other. (2) Acetylation of hydrophenols in the presence of tetralin does not yield correct results, owing probably to the presence of ketones in com. hydrophenols. (3) Hydrophenols alone in soaps can be satisfactorily detd. by steam distn. and subsequent ether extn (*C. A.* 19, 904). (4) Oxidation expts. of hydrophenols with  $\text{CrO}_3$  did not lead to any useful analytical method; such oxidation goes beyond the ketone stage, which requires 1 atom of O per 1 mol. hydrophenol, and apparently stops at the adipic acid stage, requiring 4 atoms O per 1 mol. hydrophenol, but does not reach the final  $\text{CO}_2 + \text{H}_2\text{O}$  stage, which would require 17 atoms O. P. ESCHER

The commercial preparation of neutral soft soap. A. D. STEWART AND NANI LAL BANERJEE. *Indian J. Med. Research* 12, 783-7(1925).—A cheap, practically inodorous soft soap can be manufactured from fish oil by running the oil into an excess of hot KOH fye gradually. Then the mixt. is diluted, boiled and air blown through it. The excess alkali may be neutralized by adding  $\text{NH}_4\text{Cl}$ , 28% in excess of the theoretical amt. FRANCES KRASNOW

Can small additions of rosin soaps diminish the danger of rancidity in soaps? C. BERGELL. *Z. deut. Öl-Fett-Ind.* 45, 233-4(1925).—An addn. of 1% of rosin soap prevents rancidity in soaps contg. 2% and 5% free tallow (observation for 65 days), and 3% rosin soap will prevent rancidity and prevent or retard occurrence of brown spots in soaps contg. 25% linseed-oil soap or 25% cottonseed oil soap. The rosin acts as a protective colloid toward fatty acids. P. ESCHER

## 29—LEATHER AND GLUE

ALLEN ROGERS

Progress and modern tendencies of the tanning industry. F. L. HILBERT. *Hide & Leather* 70, 5-7(1925). J. A. WILSON

The change of keratin by alkalies. M. BERGMANN AND F. STÄTHER. *Collegium* 1925, 109-10.—Treatment with Na<sub>2</sub>S decreased the cystine (calcd. from S content after HCl hydrolysis) in sheep wool and horse hair, but the destruction of the wool structure does not depend on complete decompn. of the cystine. I. D. CLARK

The bacteriology of calf-skin soaking. GEO. D. McLAUGHLIN AND GEO. E. ROCKWELL. *J. Am. Leather Chem. Assoc.* 20, 312-33(1925).—In soaking calf skins, the bacterial growth is affected by temp., duration of the operation, proportion of skin to water, and the previous treatment of the skin. J. A. WILSON

A straight-line function in the tan-wheel. ROSALIE M. COBB AND F. S. HUNT. *J. Am. Leather Chem. Assoc.* 20, 341-50(1925).—The thickness of a skin has an influence upon the fixation of Cr and acid under certain conditions of chrome tanning. J. A. WILSON

Quebracho tannin. L. JABLONSKI. *Collegium* 1925, 131.—The phthalein fusion test (*C. A.* 15, 3000) was negative with quebracho ext. which had been strongly sulfited. Treatment with  $\text{Na}_2\text{SO}_3$  causes a chem. change as well as a change in size of the particles. I. D. CLARK

Contribution to the definition and method for determining the so-called insoluble matter in tanning extracts. II. VACLAV KUBELKA AND E. BELAVSKI. *Collegium* 1925, 111-21, III. *Ibid* 247-58, cf. *C. A.* 19, 1790.—A temp. change causes a change in size of the tannin particles in an ext. and this change is often irreversible. In prep. sofn. for analysis, boiling  $\text{H}_2\text{O}$  should be used for dissolving the ext. and for filling the flask to the mark; then the flask should be immersed in boiling  $\text{H}_2\text{O}$  for 20 min. The method of cooling is important. Undercooling to  $10^\circ$ , before bringing the sofn. to  $18^\circ$ , increased the insolubles by 2 or 3%. K. and B. suggest cooling by immersing the flask to the mark in a large vessel of  $\text{H}_2\text{O}$  at  $17^\circ$ . As the concn. of a sofn. of quebracho ext. was increased (to 350 g. per l.) the amt. of insol. matter increased; but the amt. of insol. matter in sofn. of oak wood, chestnut and mimosa exts. was at a max. at some concn. between 60 and 180 g. per l. App. for measuring  $p_H$  is described and the causes of error are discussed. An increase in acidity causes an increase in the amt. of insol. matter; at  $p_H$  values above 4 the amt. of insol. matter is very small. There is a "pptn. point" at about  $p_H$  2.7 for quebracho, 1.7 for oak wood and 1.8 for chestnut, below which the amt. of insol. matter increases very rapidly as the  $p_H$  decreases. The pptn. point is not reached with weak org. acids except in the case of quebracho. The results at a given  $p_H$  were the same with different acids. As the concn. of oakwood ext. was increased from 6 to 450 g. per l. the  $p_H$  fell from 3.7 to 2.9. The use of  $\text{CO}_2$ -free  $\text{H}_2\text{O}$  for

prepg. the ext. soln. decreased the amt. of insol matter slightly. The  $p_H$  value of the soln. is very important in analysis and should be controlled,  $p_H 4$  is suggested as a standard.

I. D. CLARKE

The determination of hydrogen-ion concentration in the tannery. W. ACKERMANN *Collegium* 1925, 232-46.—A general description of app and methods for electrometric and colorimetric detn. of  $p_H$  and suggestions for application in the tannery. Data are given showing that swelling of skin is a function of  $p_H$  and not of the kind of acid.

I. D. CLARKE

Qualitative tests for tannin. Committee report. E. STIASNY. *Collegium* 1925, 142-57.—Treatment with  $NaHSO_3$  decreased the amt. of quebracho ext. salted out at  $1/1$  and  $1/2$  satn.; it did not change the % tannin found by the shake method; but increased slightly the % tannin found by the filter method, the amt. of insol matter was changed very little. Treatment of quebracho with 15% of  $NaHSO_3$  and  $Na_2SO_3$  did not change the irreversibly fixed tannin (detd. by Wilson-Kern method) but treatment with greater amts. of  $NaHSO_3$  decreased this value considerably. The difference between results by the filter and shake methods increased as the time of treatment or amt. of  $NaHSO_3$  was increased. Syntans and cellulose exts. decreased the amt. of insol. matter in exts. to which they were added. Addn. of cellulose exts. increased, Ordoval G and 2 G decreased and other syntans did not change the rate of salting out quebracho ext. solns. Syntans increased the amt. of irreversibly fixed tannin, especially if the tanning ext. contained much reversibly fixable tannin. Cellulose exts. and syntans, if added to quebracho, interfere with the Br test, cause a positive test with aniline-HCl, and a residue with cinchonine sulfate, but do not change the  $EtC_2H_5O_2$  soly. See also Stiasny and Salomon, *C. A.* 18, 1962; Laufmann, *C. A.* 18, 2441; van der Waerden, *C. A.* 19, 747.

I. D. CLARKE

Nitrosomethylurethan as a reagent for catechol tannins. W. VOGEL. *Collegium* 1925, 189; cf. *C. A.* 19, 416.—Nitrosomethylurethan is a sp. reagent for catechol tannins; it is better than Br but no advantage over  $HCHO-HCl$  is claimed.

I. D. C

Quantitative filtration analysis in use in questions of tanning chemistry. II. K. MATTHÄUS. *Kolloid-Z.* 36, 282-7(1925); cf. *C. A.* 19, 1961.—Ostwald's method of quant. filtration analysis (cf. *C. A.* 19, 1673) was used with hide powder. The liquids were  $H_2SO_4$  solns. from 0.01 N to 3.0 N and  $H_2SO_4$  contg.  $Na_2SO_4$  or chrome alum. The treatment lasted 24 hrs. or 72 hrs. and the vol. of liquid filtering off in 5, 10, 20 and 40 secs. was measured. Tables of data and graphs in which the log of the mass of the filtrate is plotted against the time of filtering are given. The curves are usually slightly convex toward the X-axis. The rate of filtration depends on the thickness of the layer on the bottom of the filtering cell, and on the clinging together of the particles. The action of chrome alum is influenced by the swelling of the hide and the strength of the acid which accompanies it. Neutral salts had a specific effect on the surface of the particles of hide and decreased swelling. The different forms in which the chromium hydroxide is deposited in the hide from different chrome liquors show themselves in the forms of the filtration curves. The strongest acid destroyed the hide fiber.

F. E. BROWN

Leather analysis. Committee report. L. JABLONSKI. *Collegium* 1925, 132-5.—Results by van der Hoeven's method for free  $H_2SO_4$  in leather (*C. A.* 16, 850), were in good agreement and reliable results were obtained in the presence of synthetic tannins and sulfo acids either alone or in the presence of  $H_2SO_4$ . Present methods of leather analysis are considered satisfactory. Since the results are used only as a qual. guide, J. considers it useless to spend time improving details of the methods but the committee should det. if the present detns. are sufficient and should revise the figures for the av. compn. of leather.

I. D. CLARKE

Report on the determination of moisture in leather. F. P. VEITCH AND T. D. JARRELL. *J. Am. Leather Chem. Assoc.* 20, 334-41(1925).—Comparison of 3 methods—oven drying in open bottles; oven drying in closed bottles through which dried air is passed; the Bidwell-Sterling toluene distn. method (*C. A.* 19, 620).

J. A. WILSON

Mechanical leather testing. G. POVARNIN. *Collegium* 1925, 169-74.—The tests are given which the lab. of the All Russian Leather Syndicate proposes to make to det. serviceability, water resistance, ability to hold nails and suitability for sewing of leather. The app. are described which will be used for detg. water penetration and ability to hold nails. Wearing quality will be detd. by rubbing the leather in an app. against quartz sand. The leather will be extd. with  $MeOH$  as well as  $H_2O$ .

I. D. C.

Artificial leather: with special reference to its manufacture from nitrocellulose. W. J. JENKINS. *Chem. Age* (London) 12, 628-9(1925).

E. H.

Forty-two occupational disease hazards in one industry: the tanning industry

as an example of the multiple hazards in industry. DOROTHY K. MINSTER. *J. Ind. Hyg.* 7, 299-304(1925). E. H.

Developments in the manufacture and testing of glue and gelatin. TH. E. BLASWENLER. *Papierfabr.* 23, Tech.-Wiss. Teil, 266-72(1925).—The manuf. and testing of glue and gelatin are briefly described with especial reference to the paper industry. A recently developed superior glue product, known as glue beads (Leimperlen), absorbs as much water in 30 min. as glue, in sheet form, does in 24 hrs. The rate of swelling is proportional to the increase in surface, which is about 1.8. The Stern theory of adhesion is discussed (cf. *C. A.* 19, 562). Increase in strength of paper sized with animal glue is dependent on the porosity of the sheet. The paper strip method of testing glue, with detn. of the tearing strength, is suggested as a useful method of evaluating glue for sizing purposes. As a rule the more slowly and uniformly a glue swells in cold water and the greater the density of the subsequent soln. heated to 60°, the better is the quality. Glue with a high viscosity is generally superior but this is not an abs. criterion of quality. J. L. PARSONS

HOWDEN, F. P.: *The Dyeing of Leather*. Wilmington, Del.: E. I. du Pont de Nemours & Co., Inc. 30 pp.

Quick tanning of fish skins. KRISTIAN BENEDEXEN. *Danish* 34,284, March 16, 1925. The skins, after soaking, lime treatment, etc., but before the main tanning process, are treated with an aq. soln. of approx. 0.5-1.0% of lactic acid, AcOH or a similar org. acid, about 3% of NaHSO<sub>4</sub> and a suitable amt. of some stain, or with a more dil. soln. of these ingredients, however in the said proportions. The bath should have a temp. of about 30°.

### 30—RUBBER AND ALLIED SUBSTANCES

C. C. DAVIS

Rubber research in 1924. MARIANNE PIECK. *Gummi-Ztg* 39, 1427-30, 1490, 1492(1925).—A review with 86 references. Correction. *Ibid* 1556. C. C. DAVIS

A further contribution to the colloid chemistry of rubber latexes. BALATA. E. A. HAUSER. *Gummi-Ztg* 39, 1165-7(1925); cf. *C. A.* 19, 1962.—Balata latex is a dispersion of particles which are chiefly spherical, are 0.5-3.6 $\mu$  in diam. and show a rapid Brownian movement. There are also many particles below 0.5 $\mu$  in size which are visible only by the ultra-microscope. If the latex is evapd, the particles flatten against one another and form a homogeneous mass. Each particle is surrounded by a thin membrane which prevents them from fusing together on evapn. Inside this membrane is a viscous liquid which renders them easily deformable but slow to recover their original shape. A tackiness of the exterior also suggests an adsorbed resinous layer. On puncturing, the viscous liquid exudes as in the case of rubber. Unlike *Hevea* particles, however, balata particles do not swell to the bursting point through absorption of C<sub>6</sub>H<sub>6</sub>. On vulcanizing in the latex form, the internal liquid solidifies and becomes elastic progressively toward the center, so that the liquid core becomes continuously smaller and finally the whole interior becomes solid. After this, evapn. does not cause a flattening of the particles and they are not attacked by C<sub>6</sub>H<sub>6</sub>. The difference in the phys. properties, including the different stress-strain curves, of raw rubber and balata is explained by the fact that in coagulated rubber the interior of the particles is still a viscous liquid, whereas the interior of balata particles is a plastic mass. The expts. confirm the hypothesis of Park (cf. *C. A.* 19, 1209) that balata particles have a 2-phase structure. The balata latex used in the expts. contained 47.71% dry substances and its acidity corresponded to 8 cc. of N NaOH per 100 cc. (phenolphthalein). The p<sub>H</sub> value was 6.4 detd. by the Sørensen method with bromothymol blue. Spontaneous coagulation occurred only when EtOH was present. Alkalies caused microscopic agglomeration and a change in color from white to red. On addn. of acids the color reverted to white. Balata latex preserved with NH<sub>3</sub> was red, was distinctly agglomerated and turned white on addn. of acids. C. C. DAVIS

Directions for a unified system of analysis of rubber. K. MEMMLER, A. HAANEN AND E. KINDSCHER. *Z. angew. Chem.* 38, 459-70(1925).—A systematic procedure for the phys. and chem. examn. of raw or vulcanized rubber is outlined, which is presented with a view to criticism and improvement. It includes detns. of d., viscosity, swelling power, artificial aging, microstructure, H<sub>2</sub>O, H<sub>2</sub>O ext., Me<sub>2</sub>CO ext., Me<sub>2</sub>CO-sol. S, true free S, Me<sub>2</sub>CO-sol. combined S, Me<sub>2</sub>CO-sol. unsaponifiable ingredients (paraffins, etc.).

$\text{Me}_2\text{CO}$ -sol. saponifiable ingredients, cellulose esters, org. accelerators, rotatory power of the rubber resins, of non-rubber resins, of saponifiable oils, fats and waxes and of the total  $\text{Me}_2\text{CO}$  ext.,  $\text{CHCl}_3$  ext., hard asphalts, reclaimed rubber, alc. KOH ext., alc. KOH-sol. S compds., proteins, phenol-resins, paraffin-insol. ingredients, inorg. fillers, fibers, bakelite, ash (qual. and quant. analysis of Pb, Ba, Hg, As, Sb, Zn, Sn, Fe, Cr, Ca, alkalies, Mg and  $\text{SiO}_2$ ), total S, inorg. combined S, S combined with rubber, Cl,  $\text{CO}_2$ , total N, glue, graphite, C black, cellulose and rubber. Data on the necessary reagents also are given. The aging test involves exposure to ultra-violet light and measurement of the changes in the  $\text{Me}_2\text{CO}$  ext. and saponifiable ingredients. C. C. DAVIS

The contraction in volume during the formation of anisotropic rubber systems by stretching. HEINRICH FEUCHTER. *Gummi-Ztg.* 39, 1167-8(1925).—A preliminary note. Crude unmilled rubber, though isotropic in its normal condition, can be rendered anisotropic by sudden elongation. Such anisotropic rubber has a greater d. than isotropic rubber, indicating that the anisotropy and the creation of elastic internal stresses are accompanied by a contraction in vol. Thus in stretching isotropic smoked sheets 500%, the d. increased from 0.937 to 0.946, a 1% contraction in vol. occurring. This anisotropy can be destroyed by heating to 50°, in which case the vol. increases to its original size. Likewise vulcanized rubber increased in d. from 0.980 to 0.985 on stretching to 600-700% (cf. Schippel, *C. A.* 14, 867). The results indicate that in stretching rubber there is a hardening or stiffening which increases progressively with the degree of stretching (cf. Feuchter, *C. A.* 19, 1207) and which may involve a crystn. of the isotropic rubber (cf. Katz, *C. A.* 19, 2144). In this case recovery after stretching would involve redissolution of the crystals. In the anisotropic condition rubber has a different soly., action with polarized light and thermal properties than normal isotropic rubber. C. C. DAVIS

Crystallized rubbers. I. L. KONDAKOV. *Caoutchouc & gutta-percha* 22, 12,666-8 (1925).—In view of the fact that Pummerer and Koch have recently described the successful prepn. of crystd. rubber (*C. A.* 18, 3737), attention is called to the work of Kondakov (cf. *C. A.* 6, 1540; 7, 273, 1298), Dubosc and Luttringer, *Le caoutchouc, sa chimie nouvelle, ses synthèses*, Paris, 1913, 545; cf. *C. A.* 9, 2096), in which polymerized isoprene or synthetic rubber was obtained in cryst. form. Similarly the view of Staudinger (*C. A.* 18, 3490), that recent work of several investigators on the reduction of rubber represents the first success attained in this problem is incorrect. A survey of the work of other investigators on the polymerization and reduction of certain hydrocarbons indicates that Berthelot (cf. *Jahresber.* 1869, 334) obtained the same product. C. C. DAVIS

Rubber latex particles. E. P. WIGHTMAN AND A. P. H. TRIVELLI. *Ind. Eng. Chem.* 17, 164(1925).—The work of Hauser on latexes (*C. A.* 19, 1962) has been confined to the properties of the particles in static equil. A cinematograph study of dild. Hevea latex by W. and T. shows that the particles have essentially the same properties when they are in Brownian movement. Their diam. is 0.2-4.0  $\mu$  and usually is 0.7-0.8 $\mu$ . They are continually being deformed by bombardment of the liquid or by each other or by local differences in surface tension. Single particles frequently divide into 2 particles and 2 particles fuse into a single one. The cinematograph method is suggested for studying peptization and coagulation. Correction. *Ibid* 323. C. C. D.

Crude-rubber testing. Rate of cure. C. W. SANDERSON. *Ind. Eng. Chem.* 16, 966-8(1924).—In detg. the rate of cure of rubber it is advantageous from the technical point of view to obtain this information without resort to a series of cures and without depending upon the uncertainties of measuring ultimate elongations and tensile strengths. For this reason the method recommended by the Crude-Rubber Comm. is essentially that of de Vries (cf. Schidrowitz, *C. A.* 14, 366; de Vries, *C. A.* 15, 2563; Whitby, *C. A.* 15, 330) except for a change in the standard point. From the stress-strain curve of the sample (rubber 100, S 10) after curing 3 hrs. at 141° the slope is detd. from the difference in the % elongation at 1.04 and at 0.60 kg. per sq. mm. divided by 2.5. The distance on the elongation axis from the standard point is then detd. For the latter 850% elongation at 840 kg. per sq. mm. is proposed (cf. de Vries), on the basis of which numerous tests show that a difference of 60 min. in the cure gives a change of 13.5 units. The rubber may be cured at 145° instead of 141° without any essential difference in character of the curves, either before or after artificial aging at 71°. C. C. DAVIS

The electrodeposition of rubber. S. E. SHEPPARD AND L. W. EBERLIN. *Ind. Eng. Chem.* 17, 711-4(1925).—The fact that dispersions of rubber in  $\text{H}_2\text{O}$ , whether natural or artificial and whether or not they contain accessory compounding ingredients, are electrically charged is utilized to deposit rubber compd. on metals or on other ma-

terials. The dispersion is first mixed with the S, accelerator, fillers and other ingredients and the whole "adsorption compd." is deposited electrolytically on the anode, the latter comprising the material to be coated. Selective deposition does not take place and the coherent layer obtained has the same compn. as the original dispersed mixt. The voltage and current d. may be varied considerably without much effect on the character of the deposit. Though the rubber compd. is inherently a non-conductor the fact that the deposit still contains intermicellar liquid allows coatings of considerable thickness to be obtained. Furthermore with adequate stirring technically uniform coatings can be obtained on objects having sharp contours. Subsequently to the coating operation and after washing and drying, the rubber may be vulcanized in the ordinary way. By first impregnating non conductors such as fabrics with an electrolyte or by graphitizing or metallizing, the process may be extended to the electrodeposition of rubber on fabrics. C. C. DAVIS

Modern manufacture of rubber adhesive plasters. RUDOLF DITMAR. *Caoutchouc & gutta-percha* 22, 12,670-1(1925).—A review, with a discussion of the phys. and chem. properties requisite in a high-grade product and the relative value of various ingredients. C. C. DAVIS

The problem of vulcanization. III. The separation of raw rubber into its gel components by diffusion. H. FEUCHTER. *Kolloidchem. Beihfte* 20, 434-48(1925); cf. *C. A.* 19, 1207.—If raw unworked rubber is immersed in certain org. solvents (aliphatic, aromatic and chlorinated hydrocarbons,  $\text{CS}_2$ , turpentine,  $\text{Et}_2\text{O}$ ,  $\text{AmOAc}$ , etc.), part of the rubber diffuses into the solvent and a gel skeleton remains behind. In the solvent this undissolved gel is a white, finely divided inelastic mass, which on evapn. gives a yellow or brown, tough, leathery, only slightly elastic mass. The latter retains with great persistency the last portions of the diffusible component and even after repeated extrn. the last of the diffusible component is not removed from the gel. The diffused rubber forms on evapn. an almost colorless, glass-clear, compact, extremely tacky mass, the elasticity of which is greater than that of the original rubber. With a small quantity of solvent it forms a clear, stable gel which in turn with more solvent forms a clear colloidal soln. exhibiting the typical phenomena of viscous liquids and the Tyndall effect. After mastication, diffused rubber has much less swelling power, gives less viscous solns. and instead of being highly elastic is very plastic. Unlike other solvents, if its  $\text{Et}_2\text{O}$  soln. is evapd., white, opaque aggregates are formed which are isotropic and which resemble colloidal crystal aggregates. This transformation to the cryst. form is not permanent after drying and on standing even at  $0^\circ$  or in an atm. of  $\text{H}_2\text{O}$  or  $\text{Et}_2\text{O}$  slow transformation back to transparent diffused rubber takes place. If the retransformed product is again dissolved in  $\text{Et}_2\text{O}$  and evapd., colloid crystn. does not recur. The limited swelling of unworked natural rubber represents an equil. which is a resultant of the differing behavior toward solvents of the 2 components. The diffusible component forms a highly elastic medium which by swelling and dissolution exerts an osmotic pressure on the insol. gel skeleton. This pressure increases the vol. of the gel until its permeability becomes so great that the dispersible component can diffuse through the gel structure. Diffused rubber which has undergone no mech. treatment represents a colloidal aggregation of rubber particles in the purest form yet obtained and is probably the first approach to pure rubber hydrocarbon yet made (cf. Pummerer and Koch, *C. A.* 18, 3737). The diffusion phenomena described are confined to the action of solvents on unworked rubber, for the swelling power of the latter decreases progressively with the amt. of working and a structureless, viscous system is formed which does not represent the colloidal structure or condition of the original rubber. C. C. DAVIS

Recent developments in rubber accelerators. J. F. SMITH. *Ind. Eng. Chem.* 16, 1024-6(1924).—A review of the characteristics and uses of org. accelerators. C. C. DAVIS

The use of the micromanipulator and other optical instruments for the microscopic study of latexes in the tropics. E. A. HAUSER. *Z. wiss. Mikrosk.* 41, 465(1924); *Gummi-Ztg.* 39, 1360-1(1925). C. C. DAVIS

Higher fatty acids and their anhydrides; rubber substitutes (HOLDE) 27.

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# CHEMICAL ABSTRACTS

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No. 17

## 1—APPARATUS AND PLANT EQUIPMENT

W. L. BADGER

Aluminium in the chemical industry. ANON. *Chem.-Zig.* 49, 571-3(1925); cf. C. A. 19, 587. E. H.

A zinc nitrate thermostat. MARTIN KRISTENSEN. *Centr. Bakt. Parasitenk.* 1 Abt., Orig. 94, 470-4(1925). JOHN T. MYERS

A sensitive glass manometer for gases which attack mercury. ALFONS KLEMENC. *J. Am. Chem. Soc.* 47, 2173-5(1925). E. J. C.

A new vacuum thermoelement. W. J. H. MOLL AND H. C. BURGER. *Z. Physik* 32, 575-81(1925).—Two thin plates of different metals, such as constantan and manganin, were silver-soldered together along an edge and drawn out in the direction of the silver union. In this way sheets were secured from 6 $\mu$  to 1 $\mu$  in thickness from which thermoelements were cut. These were mounted in a vacuum tube. They are very sensitive and register the max. e. m. f. within a few seconds when illuminated. Examples are given of the use of these thermoelements in detg. the intensities of spectral lines. H. C. U.

A simple and self-contained spectroscopic lighting unit. R. C. FREDERICK AND E. R. WEBSTER. *Analyst* 50, 234-5(1925). W. T. HALL

A handy, simple photometer for the measurement of low transparencies. ENOCH KARRER AND A. PORITSKY. *Z. tech. Physik* 6, 266-8(1925).—2 cuts. J. H. PERRY

Some applications of thermels in the measuring technic of large-scale chemical industry. F. GMELN. *Ann. Physik* 76, 198-224(1925).—(1) *O* as impurity is measured in H and in N almost instantaneously as the gas streams by, by using a catalyst and furnace (350° or so) in a side stream. The heat produced is measured by a thermel of from 8 to 24 couples, and a sensitive voltmeter. *Constant speed* of the gas, a very important factor, is secured by a series of constrictions, alternating with outlet tubes dipping in liquid, constituting overflow pressure regulators. Failure of the stream, or excessive impurity, rings an alarm. In one case the app. indicated 0.1 per mille of *O* within a minute, and rang the alarm at 0.5 per mille. (2) Variations in the composition of producer gas are continuously measured by a calorimeter which consists of a flame radiating to a thermopile. Marquardt capillaries increase and make more uniform the radiating power of the flame. The lag is about 20". W. P. WHITE

The Völcker furnace. PRADEL. *Feuerungstechnik* 13, 234-6(1925).—P. describes and illustrates an inclined-grate furnace, which has a preliminary drying shaft. The wide grate has an adjustable arrangement for equalizing the tendency toward increased combustion at the edges. The combustion space is restricted, and is elaborately baffled. A jet of air parallel to the surface of the fuel bed prevents the flames from blowing out of the door. ERNEST W. THIELE

Bisulfite as a liquid for baths. ERWIN BENESCH. *Chem.-Zig.* 49, 509(1925).—Bisulfates, made by mixing Glauber salt with H<sub>2</sub>SO<sub>4</sub> in varying amts., are recommended as substances for use in baths to be maintained at temps. above that of the water bath, as they can be employed readily in glass, porcelain and enameled vessels, and even in iron baths if kept hot. A table gives the compn. and properties of 13 such mixtures. W. C. EBAUGH

Fundamental principles of extraction and their application to extraction-apparatus design. OTTO MICHAELIS. *Z. Ver. deut. Ing.* 69, 835-9(1925).—The design of com. extn. app. is briefly considered from the standpoint of the 4 fundamental requirements of any com. extn.; (1) contact between the solvent and the material to be extd.; (2) sepn. of the solvent from the undissolved material; (3) sepn. of the solvent from the dissolved material; and (4) recovery of the solvent. Various designs of extn. vessels, stills and condensers are mentioned with which these 4 steps are accomplished. The function of auxiliary app. such as H<sub>2</sub>O separators, sediment filters, pumps and containers is outlined. A list of the more common com. solvents includes C<sub>2</sub>H<sub>6</sub>, CS<sub>2</sub>, EtOH, Et<sub>2</sub>O,

$\text{CCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{C}_2\text{H}_2\text{Cl}_2$ ,  $\text{H}_2\text{O}$ , etc. Filter presses are sometimes used in the extrn. of finely divided materials. R. L. DODGE

A simple apparatus for extracting liquids with a heavier solvent. H. SCHUMALFUSS AND H. WERNER. *J. prakt. Chem.* 110, 37-9(1925); 1 cut.—The app. resembles that described in *C. A.* 19, 1793, but the tube *R* and sack *B* are removed and the tube from *S* to *G* forks, the branch entering *G* near the top while the main tube, after entering *G*, is reduced in size and extends nearly to the bottom of *E*, to return the solvent to *S*. The soln. to be extrd. is placed in *E*, which may be heated, and the solvent drops through it from *K*. J. H. MOORE

Continuous extraction apparatus. P. A. HOUSEMAN AND C. K. SWIPT. *Ind. Eng. Chem.* 17, 830-1(1925).—The authors' continuous extrn. app. (*C. A.* 14, 65) has been modified to contain a no. of novel features, notably safety devices. Two extrn. vessels in parallel allow continuous operation. All parts are of metal. Overheating of the solvent boiling bath is prevented by a fusible link in the elec. heater line. Automatic connection through a relay cuts off current to solvent boiling bath if condenser water flow is stopped. R. L. DODGE

Apparatus for distilling off very volatile solvents. C. STIEPEL. *Chem.-Ztg.* 49, 509(1925).—Between an extrn. flask and an upright reflux condenser is fitted (ground-glass joint) a spherical receiver through which passes a vertical tube, surrounded by a non-conducting vacuum space as in a Dewar tube, to lead the vaporized solvent from the flask to the condenser. The condensate then collects in the space between the inner tube and the walls of the app. When the solvent has boiled off an attachment (all glass), like a wash bottle stopper and tubes, is inserted in place of the receiver above described, in order to facilitate drying in a vacuum or in a stream of  $\text{CO}_2$ . W. C. B.

A porous electrode for oxidations or reductions. MAX KNOBEL. *Ind. Eng. Chem.* 17, 826(1925); cf. *C. A.* 17, 2659.—Porous electrodes of Pb, Cu, Zn, Ni, Fe and Ag have been made by depositing the metal electrolytically on a porous graphite electrode while a current of air is blown through the walls of the electrode. The air is supplied through a hole passing axially through the cylindrical electrode (see Ger. pat. 109,051 (1898)). The porous, metal-coated, graphite electrodes are useful in various reactions, including the reduction of  $\text{CO}_2$  to formic acid and the oxidation of benzene to quinone. R. L. DODGE

Agitating device for determination of corrosion rate of metals. W. R. FETZER. *Ind. Eng. Chem.* 17, 788(1925).—Glass tubes, closed at one end, 30 cm. long, 4 cm. diam., bent at right angles in the middle, are attached to a board which rocks 40° twenty times a min. The horizontal closed portion of the tube contains the corroding soln. and test pieces. E. L. CHAPPELL

Auxiliary machines in a chemical laboratory. E. KUR. *Chem.-Ztg.* 49, 508-9(1925).—A plea for the protection of a lab. against noises from app. like stirring machines, grinders, pulverizers, etc., with hints for controlling a part, at least, of this nuisance. W. C. RAEUCH

Tyler electric silica still. J. C. OLSEN, W. LINDENTHAL AND I. SHERMAN. *Trans. Am. Inst. Chem. Eng.* 16, Pt. 1, 101-10(1924).—Detailed description of a still designed and constructed by S. L. Tyler, of the Thermal Syndicate, and made entirely of  $\text{SiO}_2$ , except for the heating element, which is enclosed in a  $\text{SiO}_2$  tube. Tests are given showing utilization of the elec. energy with an efficiency of up to 92%. It may be used to produce distd.  $\text{H}_2\text{SO}_4$  and other acids of very high purity and of practically any concn.  $\text{H}_2\text{SO}_4$  may be concd. to over 97%. A. PAPINEAU-COUTURE

Multi-phase motor without power loss ("Blindverbrauch"). TH. HOPPMANN. *Chem. App.* 12, 125-6(1925); 3 cuts. J. H. MOORE

Din rivet for boiler and apparatus construction, and the measuring of the rivet seam. G. HÖNNICKE. *Chem. App.* 12, 83-4, 107-8, 116-8(1925). J. H. MOORE

Apparatus for generating acetylene. W. C. GILMORE. U. S. 1,544,443, June 30  
Apparatus for separating cement dust or other solid particles from fine gases, etc. M. W. CARY. *Brit.* 227,774, Oct. 11, 1923. See U. S. 1,502,135 (*C. A.* 18, 2826)

Apparatus for separating gaseous mixtures by use of absorptive materials. E. URBAIN. *Brit.* 227,405, Jan. 9, 1924

Cleaning gas in a whirling vortex spray apparatus. W. MATHESIUS. U. S. 1,543,941-2, June 30

Venturi tube and pervious diaphragm apparatus for purifying gases. H. F. SMITH. U. S. 1,544,950, July 7.

Apparatus for washing and purifying furnace gases, etc. M. W. CARY. *Brit.* 227,501, Oct. 11, 1923.

- Apparatus for subjecting gases to catalytic synthesis under pressure. G. L. E. PATART. Brit. 227,853, Jan 17, 1924
- Container for holding and regulating volatilization of liquefied oxygen or other liquefied gases. E. F. MUELLER and C. W. KANOLZ. U. S. 1,544,854, July 7.
- Apparatus for heating air or other gases by heat interchange with hot gases. W. DYRSSEN. U. S. 1,543,909, June 30.
- Apparatus for determining density of gases by differential pressure comparisons. A. J. MALONE, J. T. FOX and J. F. J. MALONE. Brit. 227,671, March 19, 1924.
- Apparatus for distilling water, etc. G. EPPRECHT. U. S. 1,544,383, June 30.
- A combination still, water bath and drying oven for lab use
- Filter for water, etc. W. PATERSON. Brit. 228,010, Feb. 1, 1924.
- Gravel filter. W. WAGNER. U. S. 1,544,617, July 7.
- Filter with annular filtering gauze units. S. M. VIALE and ARMSYRONG SIDDELEY MOTORS, LTD. Brit. 227,550, Oct. 30, 1923
- Filters of sand or other loose materials. J. T., and J. BRANDWOOD. Brit. 227,343, May 22, 1924.
- Apparatus for oxidizing oils with air and ultra-violet light. H. SCHOFIELD. Brit. 227,212, Oct. 16, 1923.
- Apparatus for separating oil from water, etc. B. D. COMYN and W. A. WHITE. Brit. 227,544, Oct. 24, 1923.
- Apparatus for separating oil and water. H. HOCKING. Brit. 227,722, June 19, 1924.
- Apparatus for gravity separation of oil and water, etc. H. M. ALEXANDER. Brit. 227,518, Oct. 16, 1923.
- Hygrometric indicator, recorder and regulator. E. W. COMFORT. U. S. 1,544,516, June 30.
- Steam superheaters. J. RUTHS. Brit. 227,868-9, Jan 17, 1924. A pipe coil for superheating steam is heated by vapor of Hg, phenanthrene,  $C_{10}H_8$ ,  $CS_2$  or S or other substance preferably one of high b p
- Crucible. M. S. CLAWSON. U. S. 1,543,905, June 30. A crucible adapted for melting metals comprises a body of high-resistance material such as "carbon" or graphite, and a lining, formed in sections and composed of an oxide of Mg, Cr, Zr, Si, Al or Ca or similar refractory material
- Furnace adapted for melting glass, enamel, metals or other materials in crucibles. T. H. O'BRIEN. U. S. 1,545,008, July 7.
- Furnace for heat-treatment of rods or bars of metal, carbon, etc. G. M. LITTLE. U. S. 1,543,714, June 30.
- Metal-lined reinforced concrete tanks or holders for gas or liquids. Soc. ANON. ETABLISSEMENTS, ARBEL, FORGES DE DOUAI, FORGES DE COUSON. Brit. 227,652, Feb. 19, 1924.
- Tunnel apparatus for dehydrating fruits, vegetables or other materials. H. C. LORD. U. S. 1,545,000, July 7.
- Apparatus for lixivation and evaporation. C. COLLARD. Brit. 227,843, Jan 14, 1924. An app. previously described in Brit. 166,896 for extg. gelatin is modified to render it suitable for extg. other materials and for evapg. the solns. obtained
- Apparatus for selective absorption of hydrocarbons or other gases in solid absorbents. E. URBAIN. Brit. 228,094, Jan 26, 1924. A modification of the app. of Brit. 218,974, C. A. 19, 422.
- Electron-emitting cathodes. C. D. HOCKER. U. S. 1,545,256, July 7. A carrier solid at ordinary temp. but melting at higher temps. e. g. paraffin, is employed with  $BaCO_3$  and  $SrCO_3$  (separately used) or other thermionically active coating material, for coating Pt with successive coats of the carbonates.

## 2—GENERAL AND PHYSICAL CHEMISTRY

GEORGE L. CLARK AND BRIAN MEAD

- Edward Hopkins Jenkins. E. M. BAILEY. *Ind. Eng. Chem* 17, 874(1925).—A brief biography, with portrait.
- Chemistry and science in prehistoric America. J. A. BRANEGAN. *J. Chem. Education* 2, 588-92(1925).
- The American Institute of Chemists, its scope and methods. M. L. CROSSLEY. *Chem. Met. Eng.* 32, 629-31(1925).

- The new laboratories of the École Centrale des Arts et Manufactures. R. VIL-  
LERS. *La nature* 53, 14-6(1925).—A description with photographs. C. C. DAVIS.  
Correlation of lecture, recitation and laboratory work in general chemistry. C.  
A. BRAUTLECHT. *J. Chem. Education* 2, 566-75(1925). E. H.  
Observations on teaching the history of chemistry. E. F. SMITH. *J. Chem.*  
*Education* 2, 533-55(1925). E. H.  
Objectives in teaching chemistry. H. R. SMITH. *J. Chem. Education* 2, 585-7  
(1925). E. H.  
Some suggestions as to the selection of a laboratory manual for high-school chem-  
istry. W. G. BOWERS. *J. Chem. Education* 2, 605-9(1925). E. H.  
Application of the electron concept to oxidation-reduction reactions in general chem-  
istry. S. R. BRINKLEY. *J. Chem. Education* 2, 576-84(1925). E. H.  
Teaching principles of electrodeposition. W. BLUM. *J. Chem. Education* 2,  
556-65(1925). E. H.  
The Babylonian origin of alchemy. ROBERT EISLER. *Chem.-Ztg.* 49, 577-8(1925).  
E. H.

My periodic classification of the elements and the electrical constitution of atoms  
and of valence. GIUSEPPE ONDO. *Gazz. chim. ital.* 55, 149-74(1925).—In this revision  
of his periodic table (C. A. 15, 1837) which cannot be reproduced here O. has introduced  
the following changes: He has enumerated B among the metals and Sb among the metal-  
loids. Both of these are transition elements and by keeping account of the sum of the  
negative and positive valences that for B is less than 8, as in all metals, while that of  
Sb is 8 as in all metalloids. Guided by the at. no., O. was able to assign each of the  
14 metals of the rare earths its own place and included them between  $N = 58$  Ce and  
 $N = 73$  Ta. As represented Period VI is composed of 2 subperiods including the ele-  
ments from  $N = 51$  Sb to  $N = 85$  (an unknown element). Period VII begins with the  
3 emanations placed in the zero-valent group and contains the few remaining elements.  
The most important change is the introduction of the radioactive elements. In O's  
former table no account was taken of isotopy. Fajau's law, namely, that each  $\alpha$ -ray  
expelled from a radioactive element detrs in the new element that its at. wt. will be 4  
units less and a change of 2 places to the left in the periodic table and that each  $\beta$  ray  
expelled detrs a change of 1 place to the right in the table, was used in placing the  
radioactive elements. E. J. WITZEMANN

Chemical affinity and electronic structure. II. The polar link. B. H. WILSON.  
*Phil. Mag.* 49, 900-11(1925).—An attempt to relate heat of formation with the quantum  
theory of the energy changes involved in the electronic shifts assumed for polar bonds.  
The non-polar link was treated in a previous paper (C. A. 19, 1814). Half quantum  
nos. are employed. The choice of the quantum factor among several possibilities is  
rather arbitrary and constitutes the weakest point in the theory  $E_p/D = Q$ , where  
 $Q$  is the heat effect,  $E_p$  is the "energy of accommodation," given by  $E_p = A[(Z_1^2/n_1^2) -$   
 $(Z_2^2/n_2^2)]$ , in which  $A = hRcL/J$ ;  $h$  is the const. of action,  $R$  the Rydberg const.,  $L$   
Avogadro's no., and  $J$  the mech. equiv. of heat, whence  $A = 310.2$  cal.  $Z$  is the at. no.,  
and  $D = [(q_1/p_1) + (q_2/p_2) + (hZ_2/p_1)]$ , where  $p$  and  $q$  are the resp. quantum factors.  
The compds dealt with are the Li, Na and K salts of F, Cl, Br and I, halide acids and the Cu,  
Ag and Hg salts of Cl, Br and I, and AgP. The agreements with theory are very satis-  
factory. The application of the theory to the halides of bivalent metals is not satis-  
factory. S. C. I.

The atomic volume of manganese. A. N. CAMPBELL. *J. Chem. Soc.* 127, 1487  
(1925).—The at. vol. of Mn based upon new detns of  $d$  is 7.76 instead of the older  
value 7.34. This shifts the min in the at.-vol curve from Mn to Cr. If the  $d$  of Cr  
should prove to be too high there would be only 1 min. in the curve in this region at Co  
as in all other loops of the curve. G. I. CLARK

Preparation and properties of high-melting lower oxides. ERNST FRIEDRICH  
AND LIESELOTTE SITTING. *Z. anorg. allgem. Chem.* 145, 127-40(1925).—The following  
lower oxides were prepd by ignition of the higher oxides with the reducing agent shown:  
lower oxides of Ti( $H_2$ ) and Zr (C),  $V_2O_5$  ( $H_2$ ),  $V_2O_4$  (C),  $Cb_2O_5$  ( $H_2$ ),  $Ce_2O_3$  ( $H_2$ ),  $WO_3$   
(W),  $W_2O_5$  (W),  $MoO_3$  (Mo),  $Mo_2O_5$  (Mo),  $UO_2$  [brown ( $H_2$ ) and blue ( $N_2$ ) forms],  
 $U_2O_3$  (air).  $Ta_2O_5$  was not reduced. The oxides all have a hardness of about 5, and  
m. p. about 2000° (except  $WO_3$ , 1500-1600° and  $UO_2$ , 2500-2600°). They have very  
high elec. resistance except the oxides of V, W and Mo. The temp. coeffs. of resistance  
are negative. A. W. FRANCIS

The crystal structure of magnesium fluoride. H. E. BUCKLEY AND W. S. VERNON.  
*Phil. Mag.* 49, 915-51(1925).—By using the powder method  $MgF_2$  is found to have the  
symmetry of space group  $D_{2h}^{14}$ . The unit cell is a tetragonal prism with  $a = 4.660$ ,

$c = 3.078$  A. U. and  $a/c = 1.0660$ . The distance of closest approach of Mg to F is 2.07 A. U., agreeing with a calcd. value of 2.08 A. U. The structure is similar to that of rutile ( $\text{TiO}_2$ ), with which it has properties in common. S. C. L.

Crystal structure of magnesium fluoride and analogous substances. A. E. VAN ARKEL. *Physica* 5, 162-71 (1925).— $\text{MgF}_2$  belongs to the ditetragonal bipyramidal (holohedric) symmetry class;  $d_p = 3.05$ ;  $l = 3.08$  A. U.,  $d_{100} = 4.69$  A. U. The position of the atoms in the lattice is similar to that of rutile  $\text{TiO}_2$ , Mg atoms at (000) ( $1/2, 1/2, 1/2$ ), F atoms at (uu0) ( $\bar{u}\bar{u}0$ ) ( $u + 1/2, u - 1/2, 1/2$ ) ( $u - 1/2, u + 1/2, 1/2$ ),  $u$  being a little smaller than  $1/16$ . Perhaps the value for  $u = 0.403$ , which bring the 6 F atoms at equal distances from 1 Mg is the most probable. In this respect the existence of cubic  $\text{KMgF}_3$  ( $d_{100} = 4.00$  A. U.;  $\rho = 3.18$ ) with Mg in the cube center, F in the middle of the cube sides, K in the cube corners is suggestive; both lattices are very likely ionic.  $\text{PbO}_2$  also belongs to the tetragonal group of rutile structure with  $l = 3.40$  A. U. and  $d_{100} = 4.97$  A. U. A last member is  $\text{GeO}_2$ ;  $\text{SnO}_2$ ,  $\text{ThO}_2$  and  $\text{ZrO}_2$  are different.

B. J. C. VAN DER HOEVEN

X-ray examination of inner structure of various calcium carbonates. ATOMI ŌSAWA. *Sci. Repts. Tohoku Imp. Univ.* 14, 33-41 (1925).—By using a Coolidge tube with Mo anticathode and Zr filter, and an intensifying screen with Al filter on the negative, the structure of various  $\text{CaCO}_3$  samples, was found to be 1 of 2 modifications. To the calcite modification belong calcite crystal, limestone, marble, a supposed aragonite, red and white coral trees, pearl oyster, oyster, sea-ear, sea-urchin shell, crab-fish shell, fowl's egg shell, ostrich egg shell and to the aragonite modification belong 3 aragonite crystal samples, *Trubo cornutus*, *Septifer bilocularis*, an *Acropora* and a *Fava*. The Bragg aragonite model (cf. C. A. 18, 1929) is confirmed. D. S. VILLARS

Deformation and recrystallization structures of metals. R. GLOCKER. *Z. Physik* 31, 386-410 (1925).—A graphical method is given by which it is possible in the case of the rolled structure of a cubic crystal to det. from a single X-ray diagram perpendicular to the rolling direction the crystallographic indices of the 3 characteristic directions (rolling, cross section and foil normal) and the magnitudes of the scattering around the ideal orientation. This method shows that strongly rolled Ag is characterized by [112] rolling direction and (011) rolling plane, in agreement with the results of Mark and Weissenberg (C. A. 17, 2208). By heat treatment of strongly rolled Ag foils the rolled structure does not go over completely into random arrangement of the crystal grains. At a low recrystn. temp. a very stable transition state is reached with a [112] rolling direction and a (113) plane in the rolling plane, as the result of the formation of new larger crystals. "Complete" recrystn., therefore, has an entirely new meaning and a very definite criterion. G. L. CLARK

A x-ray diffraction method for the measurement of the absolute dimensions of single crystals in substances of fine-crystalline structure. N. SLYAKOV. *Z. Physik* 31, 439-44 (1925).—Like the original method of Debye and Scherrer the method depends upon the width of the X-ray powder diffraction lines. The general formula derived is  $2h = 2[\sqrt{3 \ln 2/\pi}] [1/D \cos(\theta/2)] [1/\sqrt{N}]$ , where  $2h$  is the half-intensity width,  $D = Ma$  approx. the edge length of the unit parallelepipedon, and  $N$  has a value depending upon axial ratios, axial angles and polar coordinate angles. For the cubic system  $\sqrt{N} = 1$ , so the formula reduces to  $2h = 2[\sqrt{3 \ln 2/\pi}] [1/Ma \cos(\theta_0/2)]$ , which differs by only 2% from the Debye-Scherrer formula  $2h = 2[\sqrt{\ln 2/\pi}] [1/D \cos(\theta_0/2)]$ . G. L. CLARK

Mixed crystals, agglomerations and stratified crystals. A. JOHNSEN. *Naturwissenschaften* 13, 529-33 (1925).—Review. B. J. C. VAN DER HOEVEN

The contraction constant and the affinity of solid compounds. A. BALANDIN. *Z. physik. Chem.* 116, 123-34 (1925).—The contraction const.,  $C = V/2V_0$ , where  $V$  is the at. vol. of the compd. and  $V_0$  that of its elements, equals approx.  $R-U/U_0$ , where  $U$  is the heat of formation of the substance and  $U_0$  is an empirical const. related to the heat of formation of the element in the standard state from its monatomic state. This equation is tested on 76 halides, sulfates and hydroxides, the deviations averaging about 1% except with Ag, Th and Cs salts, where it is of the order of 10%. F. R. B.

Solid solutions of compounds of elements of different valencies. G. BRUNI AND G. R. LEVI. *Atti accad. Lincei [v]*, 33, ii, 371-84 (1924).—The results of X-ray analysis confirm the conclusion reached from those of thermal analysis (cf. Tacchini, C. A. 19, 1368) that Li and Mg fluorides form solid solns., the mixed crystals undergoing decompn. at a low temp. At the ordinary temp., solid solns. of the  $\text{LiF}$  type contg. up to 20%  $\text{MgF}_2$  may be prepd. The replacement of a certain no. of  $\text{MgF}_2$  mols. by a corresponding no. of double  $\text{LiF}$  mols. causes neither appreciable change in the  $\text{LiF}$  space lattice nor

the appearance of new lines in the corresponding X-ray photographs, but, just as in other similar cases, the formation of the mixed crystals is accompanied by a slight increase in the vol. of the elementary cell.

B. C. A.

**Isomorphism between trivalent thallium and rare earth metals.** F. ZAMBONINI AND G. CAROBBE. *Atti accad. Lincei* [vi], 1, 8-14(1925).—The double sulfates  $\text{NH}_4\text{Ti}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{NH}_4\text{La}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  form monoclinic crystals, the crystallographic consts being, resp.,  $a:b:c = 1.090:1.017$ ,  $\beta = 104^\circ 26'$ , and  $a:b:c = 0.3509:1.09145$ ,  $\beta = 97^\circ 36'$ , the resp. mol vols of the 2 salts are 152.4 and 151.5. The salts form mixed crystals, the limiting soly. of the latter in the former being about 11.7%. The double sulfate,  $\text{NH}_4\text{Nd}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ , also dissolves to the extent of 11% in  $\text{NH}_4\text{Ti}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ . Unsuccessful attempts have been made to replace metals of the rare earths in the double nitrates  $\text{Mg}_2\text{R}^{+++}(\text{NO}_3)_6 \cdot 24\text{H}_2\text{O}$  by trivalent Tl. The  $\text{NH}_4$  in  $(\text{NH}_4)_2\text{Ti}(\text{SO}_4)_2$  (cf. Marshall, *Proc. Roy. Soc. Edinburgh* 24, 305-11(1902)), is capable of partial isomorphous substitution by univalent Tl.

B. C. A.

**The van der Waals equation of state. Reply to a paper by Berger.** J. J. VAN LAAR. *Z. physik. Chem.* 116, 119-22(1925); cf. C. A. 19, 1362.

F. R. B.

**Formulas for the equation of state of gases.** I. H. A. LEDUC. *Rev. gen. sci.* 36, 166-9, 197-205(1925).—On the assumption that the internal pressure of a gas is given by the equation  $\pi = Hx^2/a^2$ , where  $H$  is a const.,  $x = T_c/T$ , and  $v = V/V_c$ , and on the assumption that the terms in  $v$  have the form shown, L. derives the equation of state  $p = RT/M[v/(v-a)^2 - 3.160a(4v^2-1)/(v+a)^2]$ , where  $a = 3.86 T_c/Mp_c$ , the numerical values being empirical. This equation fits the data for  $\text{CO}_2$  within exptl accuracy in the  $p, T$  region 31-100 atm, 0-100°. It gives the proper relation between the crit. consts. and is consistent with theoretical requirements of the equations of van Laar, of Lees and of Rocard (*Bull. sci. étudiants Paris* 1924).

F. R. B.

**The rule of the four volumes.** C. PORLEZZA. *Nuovo cimento* 25, 305-6; *Publ. Inst. chim. gen. Univ. Pisa* 26, No. 56(1923).—According to Lorentz (*C. A.* 10, 1612)  $V_0/V_c = 0.27$ . From Lorentz' work it may be deduced also that  $V_f/V_c = 0.32$ , and  $V_g/V_c = 0.37$ . Therefore,  $(V_0/V_c) + (V_f/V_c) + (V_g/V_c) = 0.96$ , i. e., the sum of the reduced vol. at abs. 0°, at the abs. m. p., and the abs. b. p. is equal to 1. Whence the rule of the 4 vols., namely, the crit. vol. is equal to the sum of the vol. at abs. 0°, at the abs. m. p., and at the abs. b. p.; or  $V_0 + V_f + V_g = V_c$ . If  $V_0/V_c = 1/4$ , as is given by van der Waals' equation, there results the approx. relation,  $(V_0/V_c) + (V_f/V_c) + (V_g/V_c) = 1/4 + 1/4 + 1/4 = 1$ .

R. H. LOMBARD

**Thermal separation in gaseous mixtures.** G. A. ELLIOTT AND IRVINE MASSON. *Proc. Roy. Soc. (London)* 108A, 378-85(1925).—A study was made of the behavior of mixts. of  $\text{H}_2$ , He and  $\text{CO}_2$  taken 2 at a time and in various proportions. In all the expts a nearly const. temp. difference, approaching 500°, was maintained between 2 intercommunicating bulbs contg. the mixt., until a steady state was reached, after which the contents of each bulb were separately analyzed. It was found that: (1) In each case the constituent of higher mol. wt. becomes more concd. in the cooler part of the mixt. (2) The greatest differences in compn. between hot and cold parts of the gas exceeded 10% in mixts. of  $\text{H}_2$  and  $\text{CO}_2$ , exceeded 12% in mixts. of He with  $\text{CO}_2$ , and approached 4% in mixts. of  $\text{H}_2$  and He. The greater effect of He than of  $\text{H}_2$  in the mixts. with  $\text{CO}_2$  is significant because it occurs despite the greater mol. wt. of He; nevertheless in He- $\text{H}_2$  mixts. the He follows the "heavier-gas rule." (3) For each pair of gases there is an optimum mixt. in which the greatest sepn. occurs. This is with 55%  $\text{H}_2$  on the cold side in  $\text{H}_2$ - $\text{CO}_2$ , with 60% He in He- $\text{CO}_2$ , and with 60 to 55%  $\text{H}_2$  in He- $\text{H}_2$ . Thermal diffusion affords a very sensitive and an easily measured index of mol. repulsion or attraction.

F. L. BROWNE

**The pressure equation of an easily condensable vapor in a gas mixture, with applications to water vapor.** V. FISCHER. *Z. tech. Physik* 6, 192-5(1925); cf. C. A. 19, 917.—The equil. relations for a water-air mixt. are derived by means of Gibbs' potential. The vol. % as well as the wt. % of the satd. water vapor in air is calcd. for different pressures. The agreement with Knoblauch's data is very good. The equations derived are of general applicability to similar systems.

J. H. PERRY

**Chemistry at interfaces.** WM. HADRY. *J. Chem. Soc.* 127, 1207-27(1925).—An address summarizing H.'s researches and theories of many years, including contact potential differences, interfaces in biological systems, the thickness of the interfacial phase extending many mols. deep though exact mol. orientation is monomol., friction and lubrication. "Recent work, if anything, deepens the mystery of living matter, of how it preserves its space pattern, how it can be the *milieu* of chem. processes of peculiar and special kind, how it can maintain within itself sinks and sources of energy. It contains it is true a multitude of suspended particles, but these seem to be merely en-

closures. When they are driven to one side, as they can be by centrifuging, the material is an optical vacuum. Take the nucleus—what is it?—apparently no more than a pellicle or skin, a mere bladder contg. liquid." G. L. CLARK

The structure of surface films on water. N. K. ADAM. *J. Phys. Chem.* 29, 87-101 (1925).—A method is described for applying and measuring directly a compressive force to a surface film on  $H_2O$ , in the plane of the film. No new data are presented, but the previous results obtained by this method (C A 16, 4, 4107; 17, 3436) are arranged so that the theory regarding the mol. force-fields in surface films, especially those made up of a long-chain mol., is developed more consistently than was possible in the original papers. The theory is applied to the explaining of some of the principal points of the structure of the crystals of the fatty acids and their esters, and to the behavior of soaps.

R. H. LOMBARD

Low-temperature oxidation at charcoal surfaces. I. The behavior of charcoal in the absence of promoters. E. K. RIDEAL and WINIFRED M. WRIGHT. *J. Chem. Soc.* 127, 1347-57 (1925).—An attempt is made to measure the areas of the 3 different types of surfaces on charcoals—(1) autoxidizable fraction in which C atoms are readily disengaged with  $O_2$  as  $CO_2$ , (2) surface where O is strongly adsorbed and can be evolved unchanged or  $CO_2$  can be evolved only at very high temps., and (3) surface where  $CO_2$  may be evolved at low temps. and where adsorbed reactant O on excitation is capable either of entering into a more complete combination with the underlying C or of oxidizing a mol. of an oxidizable reactant adsorbed in juxtaposition to it. In expts to measure (1), the rate of autoxidation of charcoal specially activated was detd. by the measurement of the rate of O uptake and of evolution of  $CO_2$ . The velocity coeff is 0.013 at  $40^\circ$  and 0.023 at  $50^\circ$  independent of O pressure, and the temp. coeff 1.8. The amt. of  $K_4Fe(CN)_6$  poison adsorbed preferentially on the autoxidizable spots per 100 mg. of charcoal necessary to arrest autoxidation as detd. from the adsorption isotherms colorimetrically is  $3.6 \times 10^{-7}$  g. mol. Hence the no. of autoxidizable atoms per mg. charcoal is  $2.38 \times 10^{14}$ . The total area per mg. of charcoal detd. from the surface satn. value of amyl alc. ( $6.30 \times 10^{11}$  atoms) is 0.0266 sq. m. Hence the fraction of the surface which is autoxidizable is 0.38%. Since the rate is 0.013 cu. mm. of O per mg. of charcoal per hr., equiv. to a C consumption of  $3.51 \times 10^{14}$  atoms per hr., the av. life of the autoxidizable C atoms on the surface is 7 hrs. For the measurement of area (3) above, the oxidations of oxalic and malonic acids were studied. For the former at the max. rate, 0.105, the concn. was 0.0075 molar, the amt. adsorbed ( $x$ ) in g. mols per mg. charcoal  $3.4 \times 10^{-7}$ ; for the latter, resp., 0.060, 0.050 and  $3.9 \times 10^{-7}$ . The extent of surface catalytically active was detd. by the addn. of amyl alc. as poison whose adsorption was followed by the drop-wt. surface tension method. The amt. adsorbed sufficient to prevent oxidation is  $4.2 \times 10^{-1}$  mol. per mg. charcoal; hence the no. of catalytically active atoms is  $2.55 \times 10^{17}$  or 40.5% of the surface. The effect of O or oxalic acid concns. is expressed accurately by the equation for the rate of chem. action  $dx/dt = k(a_1P_{O_2}/v_1)[(a_2/v_2)C_{OX}]^2 = [k\sqrt{P_{O_2}C_{OX}}]/[(1 + m\sqrt{P_{O_2}} + nC_{OX})^2]$ , where  $P_{O_2}$  = rate at which  $O_2$  strikes surface;  $C_{OX}$  = rate for oxalic acid,  $v_1$  and  $v_2$  are the sp. rates of desorption of the reactants,  $a_1$  and  $a_2$  the coeffs. of reflection and  $\theta$  is the fraction of surface not covered by reactants. For small concns. of both this reduces to  $dx/dt = k\sqrt{P_{O_2}C_{OX}}$ ; if  $O_2$  is in excess  $dx/dt = kC_{OX}/\sqrt{P_{O_2}}$ ; if oxalic acid is in excess  $dx/dt = k\sqrt{P_{O_2}}/C_{OX}$ . When both concns. are large the curve passes through a max. independent of  $P_{O_2}$  or  $C_{OX}$ .

G. L. CLARK

An experimental investigation of the dynamical equation of the process of gas-sorption. D. H. BANGHAM and W. SEVER. *Phil. Mag.* 49, 935-44 (1925).—The equation  $d \log s / d \log t = \text{const. } (1/m)$  for the early stages of sorption on glass is confirmed ( $s$  is the quantity of gas absorbed at time  $t$  and  $m$  is the exponent in  $s^m = kt$ ) and is valid over a six-fold range of sorption.  $1/m$  is highly dependent on the past history of the glass and probably on min. impurities. Data beyond the range of this equation are closely represented by the formula  $\log s / (s - s_\infty) = k_1 t^{1/n}$ , where  $s_\infty$  is the limit of  $s$  as  $t$  approaches  $\infty$ . This approximates to the former equation for small values of  $s$  and  $t$ . Equations of this type appear to be applicable in a large no. of dynamical processes involving the passage of matter from a gaseous to a solid state and *vice versa*. While there are reasons for believing the phenomena are not restricted to the boundary but involve transport of matter through the solid, strong evidence is given that these laws are not those of ordinary diffusion.

S. C. L.

"Activated" graphite as a sorbent of oxygen. D. H. BANGHAM and JOHN STAFFORD. *J. Chem. Soc.* 127, 1085-94 (1925).—Graphite which takes up large quantities of H under the influence of the elec. discharge shows remarkably enhanced activity as a

sorbent for molecular O. Both graphite heated to 350° in *vacuo* for several days and such graphite exposed to H absorb O according to the equation  $s = kt^b$ , where  $s$  is the O absorbed in time  $t$  and  $k$  and  $b$  are consts. Under all circumstances  $b = 0.190$  while  $k$  varies with the past history of the graphite from 2.9 for vacuum-heated material to 3.4 for material which had been exposed to H. The change in the value of  $k$  from the low value is a measure of the induced activity. This induced activity by H is considered as a possible consequence of the crystal structure of graphite. JAMES M. BELL.

An S-form adsorption curve and its calculation. WOLFGANG OSTWALD and HERBERT SCHULZE. *Kolloid-Z.* 36, 289-300(1925); cf. *C. A.* 16, 2627; 17, 1571; and Flöröw, *C. A.* 19, 2431.—An "absorption curve" is formed by plotting  $c_0 - c$  against  $c$ , where  $c_0$  is the original concn in % of solute in the soln. and  $c$  is the concn in % of solute after adsorption has reached equil. This curve must have an S-form if its ends are at  $c = 0$  and  $c = 100\%$  and if the following 3 conditions are met: (1) Both solute and solvent must be adsorbed. The adsorbed mixt is itself a soln. (2) The g. of adsorbed material must increase according to some const. function (as Boedeker's logarithmic function) with the increasing concn. of solute. (3) The g. of adsorbed solvent must decrease in accordance with some const. function of the concn. of the solute. These conditions are usually met in adsorption from soln. When the very accurate data of Schmidt-Walker and Williams on C-AcOH-H<sub>2</sub>O or of Gustafson on C-C<sub>2</sub>H<sub>5</sub>OH-EtOH are used, the agreement is not only qual but quant. with the equation,  $(N/m)(c_0 - c) = Kc^\alpha$ ,  $(100 - c) - I(100 - c)\alpha c$ , in which  $N =$  the g. of soln.,  $m$  the g. of adsorbent, and  $K$ ,  $I$ ,  $\alpha$  and  $\alpha$  are adsorption consts of the solute, or solvent. The reason that negative adsorption and the S-form curve has not been found more frequently is that the extreme concns. have not been investigated. A test series of expts. with C-AcOH-H<sub>2</sub>O was run up to 50% AcOH, and the results were plotted after  $N/m(c_0 - c)$  was multiplied by 200. The points fall very close to the curve until the concn. of AcOH exceeds 30%, after which a deviation from the curve appears on the magnified scale. The 1-hr. shaking for equil. and the accuracy of analysis seemed satisfactory. A test for negative adsorption was made by using AcOH with several substances. All values are negative except for CCl<sub>4</sub> and Me<sub>2</sub>CO. C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub> and AcOH were tested by first wetting the charcoal with one pure liquid and then adding the mixt. Carbon wet with C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub> found  $\Delta_s = N/m(c_0 - c) = -0.183$ , calcd., -0.182. Carbon wet with AcOH found  $\Delta_s = -0.172$  (for 2 expts), calcd., -0.193 and -0.185. The system, C-AcOH-C<sub>2</sub>H<sub>5</sub>Br, was investigated from  $c = 1.139\%$  to  $c = 99.48\%$ . While the AcOH was below 15.8%,  $\Delta_s$  was positive; at all higher concns. it was negative. This is due to the supposed fact that a complex composed of 15.8% EtOH and 84.2% C<sub>2</sub>H<sub>5</sub>Br forms. This complex is adsorbed and not either individual component. When either component is in excess the excess acts as a solvent. At about this same concn. is a eutectic point and the drop no. is at a max. F. E. B.

Negative adsorption and the oxidizing effect of suspended carbon. TADEUSZ ORNO. *Kolloid-Z.* 36, 287-8(1925); cf. *C. A.* 7, 1645; Feigl, *C. A.* 16, 3422.—Ten cc of a 0.025 *N* chromate soln. and *M* NaOH were shaken with 5 g. of C and samples of the supernatant liquid were treated with HCl and KI. Samples of the original chromate-NaOH soln. were treated with HCl and KI. The soln. shaken with the C required more Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> to decolorize equal vols. of the 2 kinds of samples. This is due to negative adsorption. When 5 g. of blood charcoal was suspended in dil. NaOH and later treated with HCl, KI and starch paste, a blue color results showing the presence of hypochlorites. This shows an oxidizing effect of the suspended C. F. E. BROWN.

Progress in particle sub-division. WALTER OSTERMANN. *Farben-Ztg.* 30, 1873-4 (1925).—Brief review of the general methods of producing the colloidal state, and of the various types of colloid mills. F. A. WERTZ.

The formation of colloidal manganese dioxide in the reduction of permanganate by arsenious acid. Influence of its adsorbing power on the end-point of the reaction. MAX GELOSO. *Bull. soc. chim.* 37, 641-56(1925).—When permanganate is titrated with arsenious acid, many empirical precautions such as order of addn., rate of addn., presence of catalysts, etc., must be carefully observed. G. wishes to know why these are necessary. He showed experimentally that 1 mg. of Mn corresponded to 3.3 mg. of arsenious acid when (a) the titration was carried out at room temp., (b) 100 cc. of soln. was used, (c) the KMnO<sub>4</sub> was acidified with H<sub>2</sub>SO<sub>4</sub> in proportion to the amt. of Mn, (d) the arsenious acid was added to the KMnO<sub>4</sub> soln., (e) the end point was detd. by the color of the soln. changing to a clear green. This corresponds to the empirical formula MnO<sub>2</sub>. This could be due to mixts. (A) 11MnO<sub>2</sub>.2Mn<sub>2</sub>O<sub>7</sub>; or (B) MnO<sub>2</sub>.2MnO; or (C) 2MnO<sub>2</sub>.MnO. A would give a colored soln., so is impossible. A permanganate is unstable in an acid soln., so B is impossible. C must be tested. When the

titrated soln. stands or is heated, a ppt., apparently  $MnO_2$ , settles out. The  $MnO$  should remain in soln. as a salt of  $Mn$ . Analysis of the solo gives discordant results, and no conclusion can be made. If the concn. of acid is varied the degree of oxidation of the  $Mn$  changes. As the concn. of  $H_2SO_4$  increases the change is from  $MnO_2 \rightarrow Mn_2O_3 \rightarrow Mn_3O_4 \rightarrow MnO_2$ . Different acids have different effects. The degree of oxidation of the  $Mn$  from  $Ag_2MoO_4$  is different than that from  $KMnO_4$  and several other positive ions such as  $Zn$ ,  $Ni$ ,  $Al$  and  $Mn$  affect the oxidation of the  $Mn$  in the titration.  $MnO_2$  may be prep'd. by acidifying an alk. soln. of permanganate and arsenate. The same sort of green soln. as is formed at the end point of a permanganate-arsenite titration accompanies this reaction.  $O_2$  is evolved. The green soln. is probably due to colloidal  $MnO_2$  in both cases. The green soln. has many characteristics of a colloidal suspension. The micelles would be composed of  $n$   $MnO_2$  with adsorbed  $MnO$ . The presence of  $Mn$  salts tends to cause  $MnO_2$  to form because they furnish stabilizing  $Mn$  ions. The compn. of the solid phase is different from that of the micelles. It is impossible to assign definite formulas to the higher oxides of  $Mn$  because they vary with the method of prep'n.

F. E. BROWN

The influence of added substances on the life period of dispersoids. II. P. P. V. VEIMARN AND S. UZINO. *Kolloid-Z.* 36, 265-71(1925).—V.'s mech. prep'd. S sol was chosen for this investigation because (1) it contained no electrolytes except very small quantities of S deriva.; (2) its life period is 5-10 days, a convenient length of time for observation; and (3) a homochem. interaction was to be expected and the data would help develop that theory also. A negative S sol whose particles were 80-90  $\mu$  in diam. was prep'd by grinding 0.1 g. of rhombic S and 0.9 g. of purest sugar for an hr. in an agate mortar. The finest 0.2-0.3 g. was sep'd. out and ground for 2 hrs. longer. The finest 0.15 g. of this was agitated with 100 cc. of special dist'd.  $H_2O$ , and the sol. filtered through a hard filter. This produced a sol whose concn. was 20-30 mg. per l. and whose life period was 5-10 days. All detns. of life period were made in the same way and duplicate runs were made. The electrolytes added were  $NaCl$ ,  $KCNS$ ,  $K_2SO_4$ ,  $K_2S_2O_8$ ,  $KNO_3$ ,  $HCl$ ,  $H_2SO_4$ ,  $CaCl_2$ ,  $Ca(CNS)_2$ ,  $BaCl_2$ ,  $BaI_2$  and  $CeCl_3$ . When length of life is plotted against concn. of electrolyte, 3 types of curves result: (1) curves with 1 max. for  $NaCl$ ,  $CaCl_2$ ,  $BaCl_2$ ,  $BaI_2$ ,  $CeCl_3$ ,  $HCl$  and  $H_2SO_4$ ; (2) curves with 2 max. for  $KCNS$ ,  $Ca(CNS)_2$  and  $H_2SO_4$ (?); (3) curves with no max., that is, no concn. of electrolyte which produced a longer life than that of the untreated sol.  $KNO_3$  produced such a curve, for some unknown reason. Six graphs and 4 tables of data are given. These show that the life period at the optimum concn. increases with increasing valence of the positive ion.  $HCl$  and  $H_2SO_4$  act much like electrolytes with bivalent positive ions. Their coagulating effect would indicate that they should so act. The life curves of negative S sols are qualitatively and quantitatively like corresponding curves for dispersoid cellulose. These curves are essentially stability curves.

F. E. BROWN

The rate of coagulation of mixed colloids. K. JABLONCZYNSKI AND H. LORENTZ-ZIENKOWSKA. *Bull. soc. chim.* 37, 612-5(1925); cf. following abstr.—When suspensions of  $As_2S_3$  and  $Sb_2S_3$  were mixed the rate of coagulation followed that expressed by the equation  $\log \tan \alpha - \log \tan \alpha_0 = Kt$ . Mixts. of colloids were used:  $As_2S_3:Sb_2S_3::8:2$  and  $6:4$  and  $4:6$  and  $2:8$ . In all cases  $K$  was smaller than for either constituent. The smallest values of  $K$  were for mixts. where the amts. of the constituents were nearest equal. Each mixt. acted as a homogeneous colloid. The rates of coagulation are influenced by the varying amts. of free  $H_2S$  in the solns.

F. E. BROWN

The rate of coagulation of antimony trisulfide. K. JABLONCZYNSKI AND A. PRZEDZIECKA-JENRZEJOWSKA. *Bull. soc. chim.* 37, 608-12(1925); cf. C. A. 19, 597.—The rate of coagulation of  $As_2S_3$  follows the equation  $\log \tan \alpha - \log \tan \alpha_0 = Kt$ , where  $\alpha_0$  and  $\alpha$  are the angles of rotation of the Nicol prism in a spectrometer at the initial moment and after time  $t$ . This paper reports expts. with  $Sb_2S_3$ .  $H_2S$  was bubbled into a 0.1% soln. of  $SbOKC_2H_3O_6$  for 1 hr. and the liquid filtered off. Solns. of  $KCl$  0.125; 0.150; 0.175; 0.200 and 0.225  $N$  were used as coagulants. The observation for  $\alpha_0$  was not taken until after a period of incubation. Tables of data range from one in which  $t = 132$  min. for a change of  $\alpha$  from 52.8 to 68.7, for  $KCl$  0.125  $N$ , to another in which  $t = 0.50$  min. while  $\alpha$  changes from 54.0 to 77.0, when  $KCl$  is 0.225  $N$ . In all cases, the constancy of  $K$  is good. Expts. extending over 1 day and 3 days using the 5 concns. mentioned show that  $K = K_0 C^n$ , where  $K_0$  is the rate of coagulation for 1  $N$  soln.,  $K$  the rate at any concn.  $C$ , and  $n$  is 5 or 6. The presence of  $H_2S$  stabilizes the colloid. The const.  $K$  for  $KCl = 0.175$   $N$ , with  $H_2$  bubbling through the soln. is four fold the  $K$  for the same concn. of  $KCl$  when the  $H_2S$  had been allowed to escape but not driven out by  $H_2$ . The  $H_2S$  cannot be completely removed, even by bubbling  $H_2$  through the soln.

F. E. BROWN

Electrical conductivity and coagulating power of acids and of bases. G. Rossi AND M. ANDREANELLI. *Gazz chim ital* 55, 99-103(1925).—Experience has shown that solns of acids and bases having the same elec. cond. do not have the same coagulating power toward negative and positive colloids, resp. This property depends on many factors and cannot be expressed by so simple a law as that of Hardy. Perrin (*J. chim. phys* 3, 50(1905)) modified this law thus: The coagulation of a negative hydrosol by means of various acids is brought about by means of solns. contg the same no. of H ions and also, basic solns. that have the same coagulating power for a positive hydrosol contain the same no. of OH ions. These statements consider the phenomenon as purely elec. but if the phenomena of positive and negative adsorption described by R. that lead to neutralization of the particle and to coagulation (*C. A.* 18, 3510) are taken into account, P's statements are not adequate. Moreover the coagulating power of the same solns. of acids may become inverted in 2 different negative colloids. In fact a given soln. of HCl coagulates a soln. of  $\text{As}_2\text{S}_3$  more effectively than a soln. of  $\text{H}_2\text{SO}_4$  having the same sp. elec. cond., as that of the HCl, but the same  $\text{H}_2\text{SO}_4$  soln. has a greater coagulating power than the HCl soln. toward a colloidal soln. of Congo red. The latter observations are just the reverse of what is to be expected in terms of P's generalization.

E. J. WITZEMANN

The velocity of ice crystallization through supercooled gelatin gels. E. H. CALLOW. *Proc. Roy. Soc. (London)* 108A, 307-23(1925).—Test tubes contg. the gelatin gels at  $-3^\circ$  were seeded with minute pieces of ice. From these points ice crystals sep'd. downward through the gels at a uniform velocity. Increases in the concn. of gelatin cause decreases in the velocity of ice crystn. Such decreases are considerable for concns. of gelatin above 1% (above 2% at  $p_H$  4.75); e. g., at  $p_H$  1.50 the velocity of crystn. through 1% gel was 960 cm/hr (about half that through  $\text{H}_2\text{O}$ ) and that through a 1.5% gel was only 40 cm/hr. For lower concns. of gelatin the velocity is of the same order of magnitude as through  $\text{H}_2\text{O}$ . When the  $p_H$  was varied by means of HCl the velocity of crystn. showed a min. at the isoelec. point and a max. about  $p_H$  2.6. A similar effect was obtained with  $\text{H}_2\text{SO}_4$  but in this case the velocities were less. The presence of NaOH also increased the velocity of crystn. The curves obtained for 4% gels contg. varying amts. of HCl,  $\text{H}_2\text{SO}_4$ , or NaOH show a striking resemblance to the curves for swelling of gelatin. The presence of sufficient neutral salt caused a slight increase in the velocity of crystn. But when NaCl was added to gelatin-chloride gels there was a marked decrease in the velocity. This antagonistic effect resembles that obtained for swelling of gelatin. Opaque gels offer less resistance to the penetration of a falling body than clear ones contg. the same concn. of gelatin. It is suggested that opaque gels owe their turbidity to the presence of fibrils such as described by Lloyd. These fibrils appear to take no part in the formation of gel structure. Abnormally high results were obtained for the velocity of crystn. through gels contg. less than 2.5% gelatin in the region of the isoelec. point. These anomalies were correlated with the degree of turbidity. The velocities of crystn. through gels obtained from gelatin soln. which had previously been boiled for 6 hrs. were more rapid than through unboiled controls, thus showing that  $\beta$  gelatin does not retard the velocity to the same extent as normal gelatin.

F. L. BROWNE

The effect of light on the settling of suspensions. C. G. T. MORISON. *Proc. Roy. Soc. (London)* 108A, 280-4(1925).—Very fine soil suspensions were allowed to settle in parallel sided glass cells  $5'' \times 5'' \times 1''$ . Precautions were taken to avoid convection currents due to temp. gradients. In the absence of light the soils settle uniformly so that when viewed momentarily by transmitted light there is a continuous increase in opacity from the top of the cell downward. When exposed to light during settling the suspensions sep. into sharply defined horizontal strata. Each succeeding stratum from the top is denser than that immediately above it, but there does not appear to be any variation in d. throughout each single layer. On turning off the light the boundaries of the strata first bulge upward at the center and then disappear leaving the condition of uniform increase in d. with depth characteristic of settling in the absence of light. When illuminated with red light each stratum has a greater depth than when illuminated with blue light. Kaolin suspensions stratify similarly when illuminated but the strata are much shallower than in the case of the soil suspensions. A connection between this phenomenon and the formation of Liesegang rings is suggested. Further work is promised.

F. L. BROWNE

The relation between the Ostwald's viscosity equation and Poiseuille's law. K. MATTHIJS. *Kolloid Z.* 36, 281-2(1925); cf. Ostwald, *C. A.* 19, 2238.—By the principle of dynamic similarity, a relation is shown mathematically between Ostwald's equation,  $\eta' t = k_1$ , in which  $\eta'$  = the pressure,  $t$  = the time for a definite vol. of a gel

to flow through a capillary tube and  $k_1 = \text{a const.}$ , and Poisseuille's equation. By the use of different sizes of tubes and different concns of gel it should be possible to find a series of comparative viscosities from which the abs. viscosities of gels could be detd.

F. E. BROWN

**Solubility and size of grain.** I. D. BALAREFF *Z. anorg. allgem. Chem.* 145, 122-6(1925).—Hulet's observation of increased cond. of  $\text{BaSO}_4$  soln. on rubbing the ppt., followed by decrease to original value, which he ascribed to increased soly. of finer particles, was repeated by B., who showed that the observation might be due to an impurity of  $\text{BaCl}_2$  in the  $\text{BaSO}_4$ . It might also be due to higher soly. of damaged crystals, or of fragments broken off. Similar expts. with gypsum were inconclusive.

A. W. FRANCIS

The solubility of sulfur dioxide in water and in aqueous solutions of potassium chloride and sodium sulfate. J. C. HUNSON. *J. Chem. Soc.* 127, 1332-47(1925).—For the detn. of the soly. of  $\text{SO}_2$  in water between 10 and 90°, in aq. solns. of KCl contg. up to 30 g. per 100 g.  $\text{H}_2\text{O}$  between 10 and 90°, and in aq. solns. of  $\text{Na}_2\text{SO}_4$  contg. up to 20 g. salt per 100 g.  $\text{H}_2\text{O}$  between 20 and 50° the gas was bubbled through the solns. to satn. and these were analyzed. Details of the app. and method included the direct measurement of the total pressure for the soln. from which the partial pressure of the gas may be calcd., the complete displacement of all inert gases from the app., a method of sampling involving no change in pressure, the analysis of the sample entirely in the liquid phase, an accurate method of analysis and a check by approaching equil. from both sides. The solubilities of  $\text{SO}_2$  at a partial pressure of 760 mm. per 100 g.  $\text{H}_2\text{O}$  are: 10°, 15.39; 15°, 12.73; 20°, 10.64; 29.9°, 7.58; 40°, 5.54; 48.15°, 4.39; 60°, 3.25; 70°, 2.61; 80°, 2.13; 90°, 1.805. These are in good agreement with the results of Sims published in 1862. The solubilities in KCl solns. plotted against KCl concns. give straight lines. At 10° the soly. increases from 15.39 with 0 KCl to 25.4 with 29.9 g. KCl. The curves for soly. in  $\text{Na}_2\text{SO}_4$  solns. show distinct maxima which move to the left with decreasing temp.

G. L. CLARK

An explanation of the so-called intertraction phenomenon between solutions, and the molecular significance of negative surface tension. N. K. ADAM AND G. JESSOP. *Proc. Roy. Soc. (London)* 108, 324-31; *Proc. Roy. Soc. (London)* 98B, 206-13 (1925).—Wright (*C. A.* 15, 2889) and Schoneboom (*C. A.* 16, 4103) have observed that when certain solns. are superposed on other solns. mixing occurs not by simple diffusion but by the development of streamers or "pseudopodia," which start from the interface and make their way upwards and downwards. The phenomenon is attributed to a special force, "intertraction." S. suggests that this is a spontaneous extension of the interface due to capillary forces. A. and J. find that intertraction occurs only (1) if the solns. are placed one above the other and not side by side; (2) if there is a difference in the rates of diffusion between the solutes in the 2 solns. Quite different phenomena are observed if (a) the faster, (b) the more slowly, diffusing soln. is uppermost. Regular streaming only occurs if the more slowly diffusing soln. is uppermost; the movements when the faster diffusing constituent is above mainly occur in each layer independently, but eddies may result in a comparatively small amt. of mixing of the 2 layers. The movements are due to the destruction of the hydrostatic equil. of the layers by the diffusion of the solutes across the interface at different rates. They occur in alc. as well as aq. solns. Intertraction is not in any way due to capillary forces. Negative surface tension means that those forces of cohesion perpendicular to the interface, which act when there is positive surface tension to restrain the diffusion of mols. away from the interface, become negative. It is properly manifested in diffusion away from the body of the liquid.

F. L. BROWNE

Electrostatic forces in the diffusion of water through collodion membrane between solutions of mixed electrolytes. E. F. ADOLPH. *J. Biol. Chem.* 64, 339-68(1925).—"The diffusion of  $\text{H}_2\text{O}$  into solns. of electrolytes is relatively infrequent and slow through membranes other than those contg. non-diffusible electrolytes such as proteins. The diffusion of  $\text{H}_2\text{O}$  through gelatin-treated collodion membranes is correlated with the elec. properties of each ion in the portions of the soln. which bathe the membrane. This is particularly evident in mixed solns., where the rates of diffusion can be calcd. from the ratios of the concns. of the effective ions which are present. The predominant influence of multivalent ions in leading to diffusion is rendered very small whenever larger concns. of ions of opposite sign of charge are present. This is believed to be due to the increased elec. cond. of the diffusing soln. The diffusion of  $\text{H}_2\text{O}$  between 2 concns. of the same salt and between 2 different salts was studied. The diminution of the influence of predominant ions was in this latter case still greater than when the salts were combined in the same soln. Between solns. which differ very considerably, but within the range of

compn. of those fluids found within living organisms, no measurable diffusion through gelatin-treated collodion membranes occurs. Such ions do not, therefore, furnish potentials and currents such as are necessary to accomplish irreciprocal  $H_2O$  transport in living tissues." I. GREENWALD

The effect of a non-volatile solute on the partial pressures of liquid mixtures at the boiling point. B. H. CARROLL, G. K. ROLLIFSON AND J. H. MATHEWS. *J. Am. Chem. Soc.* 47, 1785-91(1925).—Curves of b. p. vs. vapor compn at 760 mm. for the systems  $CCl_4$ - $EtOAc$  + 0, 5 and 10% thymol;  $Et_2O$ - $Me_2CO$  + 0, 5 and 10% benzoic acid;  $CHCl_3$ - $Me_2CO$  + 0, 5 and 10% camphor;  $EtOH$ - $H_2O$  + 0, 5 and 10% acetamide;  $C_6H_6$ - $EtOH$  + 0, 5, and 10% camphor, 10% benzil, 10% resorcinol and 10% acetanilide. The partial pressure of the better solvent for the solute in question is reduced by the greater amount, although the systems as a whole obey the laws of dil. soln. Some new soly. data are presented. B. H. CARROLL

Ebullioscopic measurements in mixed solvents. B. H. CARROLL, G. K. ROLLIFSON AND J. H. MATHEWS. *J. Am. Chem. Soc.* 47, 1791-9(1925); cf. preceding abstr. and G. N. Lewis, *J. Am. Chem. Soc.* 28, 766(1906).—Ebullioscopic detns. on the first 5 systems in the preceding abstr. in a new app. with sensitive manostat. The equation of Lewis for change in b. p. of a liquid mixt. on addn. of a non-volatile solute is verified within the limits of error of other laws of dil. solns. B. H. CARROLL

Constitution of soap solutions in the presence of electrolytes. Potassium laurate and potassium chloride, Wm. C. QUICK. *J. Chem. Soc.* 127, 1401-11(1925).—Accurate data have been made of the transport of each of the constituents of a soln. contg. KCl during electrolysis. In a soln. which is wt. normal with regard to both salt and soap, the quantities of K, laurate and Cl ions transported are 0.47, 0.19 and 0.32 equiv., resp. Apparently, therefore, the undissociated soap (neutral colloid) scarcely moves in this soln. and the ionic micelle does not contain appreciable quantities of undissociated soap. This confirms previous work showing that the ionic micelle is a hydrated colloidal aggregate of simple fatty ions. Since the migration of the K ion, 0.47, is nearly the same as in solns. of pure KCl, whereas the migration no. of the Cl ion is only 0.32, only  $\frac{1}{2}$  of the total current is carried by KCl, the remaining  $\frac{1}{2}$  being carried by ionized soap (ionic micelle). Salt and soap therefore mutually diminish each other's dissociation. Even when 2.5 equivs. of salt are added to a wt. normal soln. of laurate, there is still an appreciable quantity of dissociated soap (ionic micelle). These data in conjunction with measurements of cond. and of dew-point lowering permit evaluation of the constituents present in these mixed solns. Further, they show that the hydration of K laurate in 1.0  $N_{\infty}$ -soln., where it is entirely colloidal (neutral colloid and ionic micelle), amounts to 12.8 mols. of water per equiv. of laurate. This confirms the value found by McBain and Jenkins by the wholly independent method of ultrafiltration. An improvement in the method of analysis of solns. of soap is described in which filtration is replaced by extrn. O. L. CLARK

The cause for the conductivity of casein solutions. META FISCHENICH AND M. POLANYI. *Kolloid-Z.* 36, 275-81(1925).—When 2 g. of casein is put into 100 cc. of water, the cond. of the mixt. is  $1.1 \times 10^{-4}$ . When 2 g. of casein is dissolved in 100 cc. of 0.01  $N$  NaOH soln., the cond. is  $53-58 \times 10^{-4}$  and the  $pH$  about 6. If all of the Na were present as ions, the cond. due to Na would not be more than  $40 \times 10^{-4}$ . If the 100 cc. of soln. of casein in NaOH is dild. to 1 l., the cond. increases until the Na can account for less than 50% of it. All of the cond. not due to Na has been assigned to some negative carrier. Ten cc. of a soln. of 2 g. of casein in 100 cc. of 0.01  $N$  NaOH was dialyzed in a tightly closed collodion sack under toluene (to prevent bacterial action), for 36 to 48 hrs. The soln. did not become cloudy nor contain a ppt. Detns. of the N content before and after dialysis showed no loss of N, but the cond. had fallen to about 50% of its previous value. This phenomenon might be ascribed to unknown acid salts of casein but no evidence of their existence could be found. The effect is not due to a membrane hydrolysis. Both animal membranes and collodion were used with the same results. Analysis of the external  $H_2O$  of the dialysis shows the presence of considerable org. substance. This indicates that org. salts from the casein diffuse through the membrane and cause the cond. of the external water. These salts are not casein. Neutral casein solns. in gelatin have the same conductivities as when the gelatin is not present. The casein ion takes no part in the cond. of casein solns. F. E. B.

The ionization of aromatic nitro compounds in liquid ammonia. I. M. J. FIELD, W. E. GARNER AND C. C. SMITH. *J. Chem. Soc.* 127, 1227-37(1925).—The mechanism of the ionization of the isomeric dinitro-toluenes and -benzenes in liquid  $NH_3$  has been investigated. These nitro derivs. undergo 2 distinct types of ionization, which proceed at measurable velocities. One occurs according to the equation  $R(NO_2)_2 + xNH_3 \rightleftharpoons$

$R(NO_2)_2 \cdot xNH_3 \rightleftharpoons R(NO_2^-)_{2-x} + xNH_4^+$ , and the other possibly with the production of a pseudo-acid. The former is characteristic of compds. with 2 nitro groups in the *m*-position to one another, and proceeds with a velocity which follows the relation for a reaction of the first order. The addn. compd. formed from the *m*-derivs. is blue or purple. The second type of ionization process is typical of compds. with the nitro groups in the *o*- and *p*-positions to each other, and proceeds at a rate which is independent of the concn. 3,5-Dinitrotoluene is anomalous in that it shows both types of change, and the *o*- and *p*-derivs. give slight initial conds. which may be interpreted as due to the first reaction. The max. conds. at any diln. are a measure of the degree of ionization of the nitro groups, and hence of their electronegative character. The nitro groups of the *m*- are much more negative than those of the *o*- and *p*-derivs. The Me group in the *m*-position lowers, and in the *o*- and *p*-positions raises, the negative character of the nitro group. 2,6-Dinitrotoluene forms an exception to these rules. G. L. C.

The dissociation constants of dibasic carboxylic acids, and the normal potential of the quinhydrone electrode in absolute methanol. LUDWIG EBERT. *Ber.* 58B, 175-84(1925).—The oxidation-reduction potential of the quinhydrone electrode (Billmann, C. A. 18, 1230) in abs.  $CH_3OH$  at 18° was detd. to be 724.4 millivolts; and its *N*-potential (H-ion activity = 1) with respect to the 3.5 molar  $Hg_2Cl_2$  electrode, 602 millivolts. The 1st and 2nd dissociation conds. of tartaric and suberic acids in abs.  $CH_3OH$  were detd. by Larsson's method (C. A. 17, 1572) by measuring the  $H^+$  ion activity in solns. of the acids suitably buffered by their guanidine salts. For suberic acid,  $p_1 = 9.09$ ,  $p_2 = 10.50$ ; and for tartaric acid,  $p_1 = 7.48$ ,  $p_2 = 9.50$ .  $p$  is the dissoc. no. =  $-\log$  (disso. const.). Orienting values of  $p$  are given for succinic and fumaric acids. These acids are 30-60,000 times weaker in abs.  $CH_3OH$  than in  $H_2O$ . According to Bjerrum's theory (C. A. 18, 1273) the difference  $p_2 - p_1$  depends upon 3 factors, 1 of which is inversely proportional to the dielec. const. of the solvent, and the distance sepg. the  $CO_2H$  groups in the mol. The larger value of  $p_2 - p_1$  in  $CH_3OH$ , as compared with  $H_2O$ , corresponds to the greater value of the dielec. const. of  $H_2O$  with respect to  $CH_3OH$ . The sepn. of the  $CO_2H$  groups in the mol. of these acids as calcd. from their dissoc. const. by Bjerrum's theory agrees well with the length of their mol. calcd. from X-ray detns. of the sepn. of adjacent C atoms in the diamond lattice, and from the length per C atom in monobasic paraffin acids as detd. by Langmuir by capillary chem. methods.

R. H. LOMBARD

The dissociation of weak electrolytes in water-alcohol solutions. L. MICHAELIS AND M. MIZUTANI. *Z. physik. Chem.* 116, 135-59(1925).—Changes in  $p_H$  on addition of small quantities of alc. to various org. acids were detd. The effect of alc. on all carboxylic acids is similar, benzoic acid showing a special sensitivity. If one det. the value for dissociation const. of an amino acid in an acid soln. and also in a basic soln., of the 2 values one is more sensitive to alcohol than the other.

S. B. ARENSON

The transference numbers of sodium and potassium chlorides and of their mixtures. JANE DEWEY. *J. Am. Chem. Soc.* 47, 1927-32(1925).—The transference no.  $T_K$  of K-ion in 0.2 N KCl soln. is  $0.4856 \pm 0.0005$ ,  $T_{Na}$  of Na-ion in 0.2 N NaCl is  $0.3767 \pm 0.0006$ . In mixts. of mol. ratio  $N_{KCl} = 0.296$ ,  $T_K = 0.174$ ,  $T_{Na} = 0.239$ ;  $N_{KCl} = 0.4988$ ,  $T_K = 0.275$ ,  $T_{Na} = 0.172$ ;  $N_{KCl} = 0.6002$ ,  $T_K = 0.316$ ,  $T_{Na} = 0.131$ ;  $N_{KCl} = 0.6936$ ,  $T_K = 0.357$ ,  $T_{Na} = 0.105$ . The method used was Washburn's. The analysis was by cond. and by detg. total chlorides. Temp. 25.0°.

F. R. B.

The transference numbers of solutions of mixed chlorides. Discussion of papers by Schneider and Braley and by Braley and Hall. D. A. MCINNES. *J. Am. Chem. Soc.* 47, 1922-7(1925).—An expression for the transference no. of the ions of binary mixts. of the type NaCl, KCl is derived on the assumption that the salts are equally ionized, that no complexes are present, and that the mobility of each ion is const. at any given salt concn. This equation agrees within limits of exptl. accuracy with the data of S. and B. (C. A. 17, 2218) and of B. and H. (C. A. 14, 3353). There is no evidence for the formation of ionic complexes as assumed by them.

F. R. B.

Kinetic study of the reduction of mercuric bromide by sodium formate. F. BOURGON AND J. PICARD. *Compt. rend.* 180, 1599-1602(1925).—The rate of reduction of  $HgBr_2$  by  $NaCHO_2$  was measured at 33° and 51° by the Oswald isolation method. A measured vol. of an 0.008 M  $HgBr_2$  soln. was added to measured vols. 0.11, 0.22 and 0.44 M solns. of  $NaCHO_2$ , resp. The unreduced  $HgBr_2$  present at the end of measured time intervals was detd. by reaction with standard KI soln. The results indicate that the reduction is a second-order reaction. Like the corresponding reduction of  $HgCl_2$  by  $NaCHO_2$  (cf. C. A. 13, 1551) this result is not in accord with the usual third-order formulation  $2HgBr_2 + HCO_2Na = NaBr + HBr + CO_2 + 2HgBr$ . By assuming the formation of a complex ( $2HgBr_2 \cdot HCO_2Na$ ) the apparent anomaly is explained, the reaction

then proceeding  $(2\text{HgBr}_2 \cdot \text{HCO}_2\text{Na}) + \text{HCO}_2\text{Na} = \text{HCO}_2\text{Na} + 2\text{HgBr} + \text{NaBr} + \text{HBr} + \text{CO}_2$  (cf. C. A. 18, 2634). By comparison of the velocity consts. at 33 and 51°, the temp. coeff. corresponding to 10° is 3.65. At 40°  $\text{HgCl}_2$  is reduced by  $\text{NaCHO}_2$  about twice as fast as  $\text{HgBr}_2$ . R. L. DODGE

Studies on catalytic action. XIV. Activity of reduced copper, reduced nickel, and thoria. 2. SHIGERU KOMATSU AND CHOJI TANAKA. *Mem. Coll. Sci. Kyoto Imp. Univ.* 8A, 135-45 (1925); cf. C. A. 19, 1804.—Cyclohexylamine is prepd. by reducing aniline with H at 178-180° over Ni, and pptg. it as carbonate from the ethereal soln. The free base is decomposed at 200-300° in tubes contg. the catalysts. Tables are given of the yield, including carbazole. Ni furnishes preferably diphenylamine and carbazole, Cu cyclohexylphenylamine, both from dicyclohexylamine. Th shows little activity. XV. Catalysis by reduced copper. 2. SHIGERU KOMATSU AND MASAO KURAYA. *Ibid.* 147-53.—l-Menthol is decomposed at 200-300° over Cu prepd. in 4 different ways. Oxidation and dehydration occur in all cases, varying in details. The results are given in tables. J. T. STERN

Simultaneous catalytic action of alumina and iron at high temperatures and pressures. V. IPATIEV AND N. KLIUVIN. *Khim. Promyshlennost'* 3, 6-7 (1925).—Ipatev's previous investigations disclosed the formation chiefly of high boiling polymethylene compds. from ethylene hydrocarbons at 400-500° in the presence of  $\text{Al}_2\text{O}_3$ ; however, low-boiling polymethylene compds. were obtained from ethylene in nascent state, generated by heating EtOH in an iron vessel at high pressures, in the presence of  $\text{Al}_2\text{O}_3$  for 6 hrs., at 530-40°. Of the 2 layers formed, the upper oily one contained polymethylene compds. only, after extn. with  $\text{H}_2\text{O}$ ; the lower one represented an aq. soln. of  $\text{Me}_2\text{CO}$  and  $\text{Me}_2\text{CHCH}_2\text{OH}$ . The aq. ext. contained  $\text{MeCHO}$ ,  $\text{Me}_2\text{CO}$ ,  $\text{MeCHCH}_2\text{OH}$ ,  $\text{MeEtCO}$ ,  $\text{MeEtCHOH}$ , probably acetal. Analysis of gases formed during reaction gave 16-20%  $\text{CO}_2$ . A thorough discussion tries to account for the formation of the various compds. H. BERNHARD

Negative catalysis in oxidation reactions. N. R. DHAR. *Z. anorg. allgem. Chem.* 144, 289-303 (1925); cf. C. A. 16, 1038, 1691.—On the basis of previously described expts. negative catalysis is considered possible in oxidation reactions wherever the catalyst is easily oxidized. Retardation in reaction rate is attributed in many cases to the formation of complexes by the oxidation catalyst and the anti-catalyst. A. G.

Dehydrogenation and autoxidation. Their relation to one another. W. MANCHOT AND H. GALL. *Ber.* 58B, 486-92 (1925).—According to Wieland (C. A. 17, 775) Pt (or Pd) behaves not as a catalyst but as a reacting substance in the dehydrogenation of hydroquinol; Willstätter (C. A. 15, 2077), however, believes that O retained in the metal imparts catalytic activity. With scrupulous care M. and G. have tried O-free Pt with hydroquinol and find that it is dehydrogenated and that the reaction is reversible. They agree with Wieland's view that autoxidation occurs in 2 steps; first dehydrogenation by the catalyst and afterwards oxidation of the H. JAMES M. BELL

The mechanism of catalytic decomposition. F. H. CONSTABLE. *Proc. Roy. Soc. (London)* 108A, 355-78 (1925).—Reactions of alics. with Cu catalysts are considered. Chem. reaction takes place in a unimol. layer, in which the alic. mol. is oriented with the  $\text{CH}_2\text{OH}$  group in contact with the Cu surface. It is predicted that the velocity of dehydrogenation of all primary alics. should be equal. This has been verified exptly. The mechanism of the change is the loss of neutral H-atoms, the energy of activation becoming the energy of oscillation of the H-atom of the OH group. The second H atom is automatically released with the mean kinetic energy characteristic of the temp. Activation of the alic. mol. by the catalyst consists in increasing the distance between the H-atom and the O atom in the OH group. Quant. treatment on this basis leads to an equation which is not in agreement with expt. The source of this discrepancy lies in assuming that the whole of the surface is active. The conception of activation increasing the distance between the H- and the O atom in the OH group leads to the idea of a "reaction center." At these areas the adsorbed alic. mol. is situated over some characteristic group of Cu atoms. The work of Taylor, of Pease, and of Armstrong and Hilditch is summarized. Application of the theory of probability to the problem of the center of activity shows that the proportional frequency of centers with heat of activation,  $\epsilon$ , is connected with  $\epsilon$  by an exponential relation. The periodic relation between the catalytic activity of Cu and the temp. at which the Cu was produced by reduction from oxide, has been split up into a general falling-off of activity, due to sintering of the centers at the instant of reduction, and a random periodic variation accompanied by change in the temp. coeff. of the reaction. Study of this latter change enables the consts. in the distribution formula to be evaluated. The reaction velocity

expression finally deduced takes the form  $e^{-a/RT} C_T S e h a / h - (1/RT) \sigma$ . This equation is in accord with experience insofar as it can be tested. F. L. BROWNE

Thermal decomposition of ammonia upon various surfaces. C. N. HINSHELWOOD AND R. E. BURK. *J. Chem. Soc.* 127, 1105-17(1925).—Up to the highest temp. reached in a silica vessel, 1050°, there is no evidence of decompn. of  $\text{NH}_3$  other than at the surface. Results in general agreement with those of Bodenstein and Kranendieck (*Z. phys. Chem.* 29, 295(1899)) were obtained but certain discrepancies were observed between the two sets of results. It appears that the mode of adsorption of  $\text{NH}_3$  on silica is by means of the H atoms and that the adsorption is very sensitive to the exact spacing of the silica mols. W is the most efficient catalyst, the reaction at its surface is almost of zero order with respect to  $\text{NH}_3$  and uninfluenced by the products of reaction. The catalyst is extremely const. in activity. The reaction on surfaces of Pt and silica is of the first order with respect to  $\text{NH}_3$  and strongly retarded by H. The retarding influence of H obeys a different law in the two cases. The retarded reaction on Pt has a very much greater temp. coeff. than the very much more rapid and unretarded reaction on W, indicating that the temp. coeff. of the former reaction is largely detd. by the freeing of the surface from H as the temp. increases. JAMES M. BELL

Oxidation of acetaldehyde. II. L. REINER. *Z. anorg. allgem. Chem.* 141, 363-74(1925); cf. *C. A.* 17, 2529.—When solns. of  $\text{AcH}$  and  $\text{H}_2\text{O}_2$  are mixed, heat is evolved owing to the formation of diacetaldehyde hydroperoxide  $2\text{AcH} + \text{H}_2\text{O}_2 \rightleftharpoons (\text{AcH})_2 \cdot \text{H}_2\text{O}_2$  (1). At 0° this compd. is fairly stable, but dissociates rapidly on heating the soln. The velocity of oxidation of  $\text{AcH}$  by  $\text{H}_2\text{O}_2$  increases with increasing concn. of aldehyde, but is little affected by the amt. of  $\text{H}_2\text{O}_2$ , provided that the ratio  $\text{H}_2\text{O}_2/\text{aldehyde}$  is greater than 0.25:1; a large excess of  $\text{H}_2\text{O}_2$  slightly retards the oxidation. The amt. of  $\text{AcOH}$  produced is usually greater than that corresponding with the  $\text{H}_2\text{O}_2$  used up, and the amt. of this excess increases with the abs. concn., but is unaffected by the ratio  $\text{H}_2\text{O}_2/\text{aldehyde}$ . These results are accounted for if the diacetaldehyde hydroperoxide produced in (1) combines with aldehyde according to the reaction  $(\text{AcH})_2 \cdot \text{H}_2\text{O}_2 + \text{AcH} \rightleftharpoons (\text{AcH})_3 \cdot \text{H}_2\text{O}_2$  (2). This second additive product is then oxidized directly by mol. O to  $\text{AcOH}$ :  $(\text{AcH})_3 \cdot \text{H}_2\text{O}_2 + \text{O} \rightarrow 3\text{AcOH} + \text{H}_2\text{O}$  (3). The mol. O required in (3) may be obtained either from decompn. of the  $\text{H}_2\text{O}_2$  or from the air, and the excess of  $\text{AcOH}$  referred to above is greatly reduced if O is excluded from the reaction vessel. The retarding effect of a large excess of  $\text{H}_2\text{O}_2$  is due to its reducing the concn. of free aldehyde owing to the mass-action effect in equation (1). The oxidation may be regarded as an autooxidation of diacetaldehyde hydroperoxide,  $\text{AcH}$  being the acceptor; on the basis of the theory of Goard and Rideal, *C. A.* 18, 1937, the oxidation potentials are in the order  $(\text{AcH})_3 \cdot \text{H}_2\text{O}_2 > \text{AcH} > (\text{AcH})_2 \cdot \text{H}_2\text{O}_2$ . The autocatalytic effect of  $\text{AcOH}$  previously reported (Reiner, *C. A.* 17, 2529) is incorrect. B. C. A.

Induced oxidations and their mechanism on the basis of the formation of ions in chemical reactions. A. N. DEV AND N. R. DRAR. *Z. anorg. allgem. Chem.* 144, 307-12(1925); cf. *C. A.* 18, 3520, 3609.—S. sugars,  $\text{EtOH}$ , starch, sodium tartrate or arsenite, etc., are oxidized at room temp. by passing air through their solns. contg. finely divided  $\text{Cu}$ ,  $\text{Cu}_2\text{Cl}_2$ ,  $\text{Cu}_2\text{O}$ ,  $\text{Zn}$ , or yellow P. Metallic  $\text{Cu}$  dissolves in solns. of these substances in the presence of O as the result of formation of  $\text{CuO}$  and its further reaction to form a sol. complex. Its power to dissolve in solns. of  $\text{NH}_4\text{NO}_3$ , even in the absence of O, is attributed to the presence of  $\text{HNO}_2$ . Induced oxidations are considered as due to activation by emitted ions. ARTHUR GROLLMAN

Studies on reaction in the solid state. V. D. BALAREFF. *Z. anorg. allgem. Chem.* 145, 117-21(1925).—Reply to Hedvall and Heuberger (cf. *C. A.* 19, 1526). The interaction of  $\text{BaO}$  and  $\text{SrO}$  with sulfates is due to molten hydroxides on the surface; but  $\text{CaO}$ , whose hydroxide is dissociated completely at the reaction temp., reacts only with the dissociated  $\text{SO}_3$ .  $\text{Fe}_2(\text{SO}_4)_3$  fumes with loss of  $\text{SO}_3$  even at 300°.  $\text{CaO}$  fails to react with  $\text{MnO}_2$  or  $\text{SiO}_2$  at 950° in contrast with  $\text{BaO}$  and  $\text{SrO}$ .  $\text{Ca}(\text{OH})_2$  dissociates at 450°,  $\text{Sr}(\text{OH})_2$  at 700°, and  $\text{Ba}(\text{OH})_2$  at 900°. A trace of  $\text{H}_2\text{O}$  catalyzes the interaction of  $\text{BaO}$  and  $\text{CaCO}_3$  because the  $\text{Ba}(\text{OH})_2$  reacts, and unchanged  $\text{BaO}$  dehydrates the  $\text{Ca}(\text{OH})_2$  formed.  $\text{BaO}$  and  $\text{SrO}$  are so hygroscopic that "dry" samples cannot be assumed to be anhydrous. The former is more hygroscopic than  $\text{P}_2\text{O}_5$ . Most reactions between solids begin at lower temps. if slightly moistened, but no quant. relation is yet possible.

The chemical mechanism of the reactions of solid substances. WILHELM BILTZ. *Naturwissenschaften* 13, 500-6(1925).—The heat of reaction  $Q$  for the incorporation of substances like  $\text{NH}_3$  or  $\text{H}_2\text{O}$  in the space lattice of a solid salt (formation of ammoniates and hydrates) consists of a part  $E = U_2 - U_1$  (lattice energies), necessary for the expansion of the lattice and depending on the nature of the salt, and a part  $A$ , the energy

A. W. FRANCIS

liberated by the combination of the added component with the lattice cation.  $E$  can be expressed Born-Landé and Grimm approx. as  $E = U_0[1 - \pi/(n-1)\sqrt{D}]$ ;  $U_0$  is the original lattice energy,  $D$  the expansion (quotient of mol. vols. before and after),  $n$  is the exponent of the repulsion force (Born) at small distances. From this equation  $E$  has been calcd. for several ammoniates and hydrates and compared with  $A (=E + Q)$ ; plotted as functions of  $\pi$ , the no. of  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  mols. resp., the  $E$  curve is slightly S-shaped, the  $A$  curve is nearly straight. Several qual. conclusions can be drawn from these curves. From the low mol. vol. of  $F$  it follows that  $E > A$  for  $\text{CaF}_2$  (no  $\text{NH}_3$  compds. insol. in water);  $\text{NaCl} \cdot 5\text{NH}_3$  is the only stable ammoniate ( $Q/m$  maximal), etc. The possibility for polyhalide, polystilide and thiohydrate formation depends on the dipole strength of the additional component;  $\text{H}_2\text{S}$  can only be taken up in a mol. lattice ( $E_{\text{H}_2\text{S}}^{\text{mol.}} > A_{\text{H}_2\text{S}} > E_{\text{H}_2\text{S}}^{\text{ionic}}^{\text{mol.}}$ ). Compds. like  $\text{NiF}_2$  are only able to add  $\text{NH}_3$  after the way has been prep'd. by one  $\text{H}_2\text{O}$  mol. (aq. compds.). Hydration of gypsum, silicates and the swelling of org. substances are discussed along similar lines.

B. J. C. VAN DER HOEVEN

Equilibria in the systems ammonium chromate, ammonium sulfate, and water, and ammonium chromate, potassium chromate, and water at 25°. SHINTARO ARAKI, *Mem. Coll. Sci. Kyoto Imp. Univ.* 8A, 213-22 (1925).—The system  $(\text{NH}_4)_2\text{SO}_4 + (\text{NH}_4)_2\text{CrO}_4 + \text{H}_2\text{O}$  is analyzed in 14 different compns. by detg. the chromate and  $\text{NH}_3$  in soln. and the residue. Similarly the system  $(\text{NH}_4)_2\text{CrO}_4 + \text{K}_2\text{CrO}_4 + \text{H}_2\text{O}$  is investigated in 27 points. The results are given in tables and curves.

J. T. STERN

The dissociation of auric chloride. MARC PETIT, *Bull. soc. chim.* 37, 615-23 (1925).— $\text{AuCl}_3 \rightleftharpoons \text{AuCl} + \text{Cl}_2$  has been supposed to represent a reversible reaction taking place when  $\text{AuCl}_3$  is heated. The vapor of  $\text{AuCl}_3$  contributes to the observed pressure. First the total pressure over  $\text{AuCl}_3$  at various temps. was detd. by heating  $\text{AuCl}_3$  in an evacuated system connected to a manometer in which the Hg was protected by  $\text{H}_2\text{SO}_4$ . Const. temps. were provided by using the b. p.'s of  $\text{H}_2\text{O}$ ,  $m$ -xylene,  $\text{C}_6\text{H}_5\text{NH}_2$ , benzyl alc., anethole, and eugenol. The temps. and corresponding total pressures in mm. of Hg are 100°, 7; 135.5°, 11; 181°, 61.2; 202°, 154.5; 229°, 424.2; 251°, 808.7. All pressures were taken with rising temps. They are reproducible. But when cooled to room temps. the pressures did not decrease as would be expected but remained in order 3-4 mm.; 8-9 mm.; 39-49 mm.; 87-99 mm.; 220, or 253, or 300 mm.; and 520 or 534 mm. When one of the cooled tubes was reheated the pressure returned to the same value as at the first heating, but each successive cooling showed a higher pressure after cooling. Some tubes stood as long as 6 weeks without any further decrease in pressure. This may be explained by assuming (1) that inactive  $\text{AuCl}$  forms when the tube is heated and its amt. increases with each heating or (2) that crystals of  $\text{AuCl}$  are covered with a layer of  $\text{AuCl}_3$  impenetrable to  $\text{Cl}$  and thus prevent the reversal of the reaction. A layer of  $\text{AuCl}_3$  actually covers a core of  $\text{AuCl}$  and may be dissolved off by  $\text{H}_2\text{O}$ . By heating  $\text{AuCl}_3$  in the smaller of two glass compartments connected by a constriction and condensing the vapor contained in the larger, the vapor pressures of  $\text{AuCl}_3$  were detd. to be 181°, 9.7 mm.; 251°, 24.6 mm.; 326°, 67 mm. Then the pressures of  $\text{Cl}_2$  are: 100°, 5.8 mm.; 135.5°, 7.5 mm.; 181°, 51.5 mm.; 202°, 142 mm.; 229°, 105.6 mm.; 251°, 784.1 mm. By substituting in the Clapeyron equation  $Q = (1.98)/(1000)(T/T' - T') \log p/p'$ , the heat of formation of  $\text{AuCl}_3$  from  $\text{AuCl}$  and  $\text{Cl}_2$  was found to be 20.6 cal. at about 190°, and to decrease as temp. changed in either direction to 16.8 cal. at about 160°, and 15.6 cal. at 240°. Concordant pressures can be obtained only by rising temps. and the reaction does not appear to be reversible but the application of the Clapeyron equation gives consistent results. F. E. BROWN

Ternary system molybdenum-nickel-silicon. PRAUSCH, *Z. Metallkunde* 17, 48-52 (1925).—Besides the binary compds.  $\text{MoSi}_2$ ,  $\text{MoSi}$ ,  $\text{MoNi}$ ,  $\text{NiSi}$ ,  $\text{NiSi}_2$ , and  $\text{Ni}_3\text{Si}$ , the system  $\text{Mo-Ni-Si}$  contains 2 ternary compds.  $\text{Ni}_3\text{MoSi}$  and  $\text{Ni}_4\text{MoSi}$ . The former is stable at all temps. below 2100°, when it melts unchanged, but the latter decomposes below 850° as follows:  $2\text{Ni}_4\text{MoSi} = \text{Ni}_3\text{MoSi} + \text{Ni}_3\text{Si}_2 + \text{Ni}_3\text{Si}$ . The silicide,  $\text{Ni}_3\text{Si}$ , forms a eutectic with the stable ternary compd. All the alloys in this system with the exception of those rich in  $\text{Ni}$  and consisting of homogeneous mixed crystals are very hard and brittle.

B. C. A.

Ternary system chromium-nickel-molybdenum. E. SIEDSCHLAG, *Z. Metallkunde* 17, 53-6 (1925).—No ternary compds. are formed in this system, but there is evidence of the formation of a ternary eutectic contg. between 5 and 10%  $\text{Ni}$ . The structure of the alloys rich in  $\text{Ni}$  consists of a homogeneous mixed-crystal phase, but all other alloys contain 2 or 3 phases consisting of the compd.  $\text{MoNi}$ ,  $\text{Mo}$  contg. small quantities of  $\text{Ni}$  and  $\text{Cr}$  in solid soln., and the homogeneous mixed-crystal phase. The alloy contg.

60% Ni, 20% Mo, and 20% Cr is only very slightly attacked by hot HCl or by hot dilute  $H_2SO_4$  and unattacked by solns. of the alkali hydroxides. B. C. A.

The system chromium-hydrogen. G. F. HÜTTIG and FRITZ BRODEKORF. *Z. anorg. allgem. Chem.* 144, 341-8(1925).—The mode of combination of H in Cr, prep'd. by electrodeposition, was studied by detg. the pressure of H over the system Cr-H at various temps. Conclusion: The H exists in an unstable, irreversible combination. It is given off slowly at lower temps., rapidly above  $55^\circ$ , and practically all eliminated at  $300^\circ$ . The pressure-temp. curves are not accurately reproducible. As high as 0.45% of H may be held in this combination. X-ray spectroscopic studies show a similarity in the lattice arrangement between pure Cr and Cr-H, whence it is concluded that the H merely penetrates into the interspaces of the lattice, giving a homogeneous supersatd. soln. of H in Cr. The  $d_{11}$  of electrolytic Cr is  $7.138 \pm 0.003$  and at  $-50^\circ$  is  $7.156 \pm 0.001$ . ARTHUR GROLLMAN

The rule of the three temperatures. C. PORLEZZA. *Nuovo cimento* 25, 291-303; *Pub. Inst. chim. gen. Univ. Pisa* 25, No. 55(1923).—Values of  $T_F$  (abs. m. p.),  $T_B$  (abs. b. p.), and  $T_C$  (abs. crit. temp.) are tabulated for about 130 substances (inorg., org., and elements), and show that the relation  $(T_F/T_C) + (T_B/T_C) = 1.04$ . Lorentz' work (C. A. 10, 1612) gave the value 1.08. It is concluded that the sum of the abs. temp. of fusion and of boiling is equal to the abs. crit. temp., verifiable to about  $\pm 10^\circ$ . The expression,  $T_F + T_B = T_C$ , may be derived directly from the theory of corresponding states, and is not necessarily a special case of Prud'homme's relation,  $[T_F(T_C - T_F)]/[T_B(T_C - T_B)] = \text{const.}$  (C. A. 15, 784). Of the two approx. expressions,  $(T_F/T_C) + (T_B/T_C) = 1/2 + 1/2 = 1$ , or  $= (1/2)(1/2) + (1/2) = 1.11$  (Lorentz), the former is nearer the mean presented by the data. R. H. LOMBARD

Freezing points of organic compounds which can be used as fixed points for low temperatures in calibrating thermometers. JEAN TIMMERMAN. *Communications from the Phys. Lab. of Univ. of Leiden* Supplement No. 51b, 35-42(1925).—Crit. comparison of the results obtained by F. Henning (C. A. 8, 1230), T. van der Horst and H. K. Onnes (C. A. 16, 1594) and Keyes, Townshend and Young (C. A. 17, 667-8), as regards possible errors due to thermometer used, method of cooling, and purity of the compds. T. suggests the following f. p.:  $CCl_4$  ( $-23^\circ$ ),  $PbCl_2$  ( $-45^\circ$ ),  $As_2O_3$  ( $-69^\circ$ ),  $C_2H_6$  ( $-95^\circ$ ),  $Et_2O$  ( $-116^\circ$ ) and isopentane ( $-160^\circ$ ), which should be det'd. to within  $\pm 0.1^\circ$ . Detns. with an accuracy of  $\pm 0.01^\circ$  would involve tremendous difficulties. A. PAPINEAU-COUTURE

Possible limits for the heat of dissociation of oxygen. O. R. WULF. *J. Am. Chem. Soc.* 47, 1944-5(1925).—The heat of the reaction  $O_2 = 2O$  is between 56,400 and 137,400 cal. This is based on Hopfeld's spectroscopic value of 13.56 v. for the reaction,  $O = O^+ + e^-$  and on an interpretation of observations of Smyth and of Lockrow and Duffendack that no ions are formed below 16.0 v. while new lines appear in the low voltage at 19.5 v. F. R. B.

An improved differential method for the exact determination of specific heats of aqueous solutions; including results for various salts and organic acids. T. W. RICHARDS and F. T. GUCKER. *J. Am. Chem. Soc.* 47, 1878-93(1925).—The heat capacity and  $d$ . of the following solns. were measured at temps. from  $14^\circ$  to  $22^\circ$ :  $HCl.H_2O$ ,  $25H_2O$ ,  $NaCl.H_2O$ ,  $25H_2O$ ,  $H_2C_2O_4.H_2O$ ,  $25H_2O$ ,  $NaHC_2O_4.200H_2O$ ,  $Na_2C_2O_4.50H_2O$ ,  $H_3C_2O_4.25H_2O$ ,  $NaH_2C_2O_4.50H_2O$ ,  $Na_2C_2O_4.50H_2O$ ,  $NaOH.25H_2O$ . The calorimetric method was Joule's; twin adiabatic calorimeters were used. Temps. were measured with a thermel, which was calibrated against a Hg thermometer. Accuracy 0.01%. The true sp. heats of most of the soln. show a minimum which differs for the various solns. F. R. B.

Influence of the variation of the coefficient of viscosity with temperature on the specific heat of solutions. NICHOLAS DE KOLOSSOWSKY. *Bull. soc. chim.* 37, 605-8 (1925); cf. C. A. 19, 1645.—The specific heat  $k$  of a dil. aq. soln. of an org. substance may be represented by the equation  $(1) k = (18\mu + 2\pi + 3)/(18\mu + M)$ , where  $\mu$  is the no. of mols. of  $H_2O$  per mol. of solute,  $\pi$  the no. of atoms per mol. of solute, and  $M$  the mol. wt. of the solute. Exptl. data showing the accuracy of this equation for solns. of urea, acetamide, dextrose,  $HCO_2H$ ,  $(CO_2H)_2$  and citric acid will soon be published. This equation is closely related to the ordinary additive law, so solns. such as those of alcs. which show sp. heats considerably higher than those indicated by the additive law are not calcd. until a correction factor is applied as described in this paper. If the viscosity of soln. is greater than that of the solvent, and if the viscosity of the two approach each other with increasing temp., then there will be less energy spent in setting up viscosity as the temp. rises. This will be measured by the expression  $d(\eta_0 - \eta)/dT$  where  $\eta_0$  = the abs. coeff. of viscosity of the pure solvent,  $\mu$  that of the soln., and  $T$  the abs. temp.

When this is multiplied by 350 (obtained empirically) and added to equation 1, specific heats for the following substances are given first as calcd, second as exptl. detd.  $\text{CH}_3\text{OH}$ , 0.991, 1.003;  $\text{C}_2\text{H}_5\text{OH}$ , 1.011, 1.010;  $\text{C}_2\text{H}_5\text{OH}$ , 1.020, 1.022;  $\text{C}_2\text{H}_5\text{O}_2$ , 0.985, 0.987;  $\text{C}_2\text{H}_5\text{ON}$ , 0.976, 0.976. The corrective term  $350 d(\eta - \gamma)/dT$  varies from 0.074 to 0.005 in this series of values.

F. E. BROWN

The heats of dissociation of oxygen and nitrogen molecules. A. EUCKEN *Ann* 440, 111-21(1924).—Various considerations, especially the increase of the sp heat at high temps, lead E. to believe that the heats of dissociation of the diatomic O and N mols are probably somewhat larger than 400 cal.

J. H. PERRY

Freezing points of hydrofluoric acid. J. D. C. ANTHONY AND L. J. HUDLESTON *J. Chem. Soc.* 127, 1122-8(1925).—The f. ps of  $\text{HCl}$  solns in  $\text{H}_2\text{O}$  are detd for 0.025 to 4  $M$  solns, and the activities calcd. The postulate that  $\text{HF}$  gives rise to complex ions,  $\text{HF}_2$ , in addition to simple ions receives confirmation and the compn of the acid worked out on that assumption (together with that of the validity of the law of mass action applied to the concns.) is supported. No appreciable quantity of double mols  $\text{H}_2\text{F}_2$  appears to exist.

JAMES M. BELL

Melting point and vaporization of graphite. E. RISHKEVICH *Z. Elektrochem* 31, 160(1925).—A correction to a previous paper (see *C. A.* 19, 1513).

H. G.

The dielectric constants of some liquids and their variation with temperature. I. G. E. BELL AND F. Y. POYNORON. *Phil. Mag.* 49, 1063-72(1925).—The application of valve-maintained oscillatory circuits to the measurement of the dielec const of castor, olive and linsed oils, with special reference to variation with temp. A linear relation holds in each case. Some of the difficulties of working with valve-maintained oscillatory circuits and the precautions taken to ensure steadiness are discussed in some detail. This work is being extended to other liquids, and also over greater ranges of temp.

S. C. L.

Measurement of dielectric constants of liquids. HERBERT HARRIS. *J. Chem. Soc.* 127, 1049-69(1925).—Alternating current bridge methods of detg the dielec consts of liquids are discussed critically and experimentally. The dielec consts of specially purified liquids are detd with an accuracy beyond any previously attained. The following consts are for 25°: benzene, 2.2482;  $\text{CCl}_4$ , 2.219;  $\text{CHCl}_3$ , 4.6417;  $(\text{CH}_2\text{Cl})_2$ , 10.131; *o*-nitrotoluene, 26.066; nitrobenzene, 34.093.

JAMES M. BELL

Influence of gas content on the electrical resistance of a wire. TH. SEHL. *Z. Physik* 32, 333-5(1925).—The existing exptl data on the effect of gas content on the resistance of a wire can be explained by the Lorentz theory, if one assumes that the gas is uniformly distributed through the metal, its effect is to increase the total no. of collisions of the electrons with the atoms. The resistance is a function of the gas content per unit vol and depends only on the quantity and not the kind of gas. Further work is being done to see whether it is possible to show whether H is present in the at. or ionized form.

H. C. U.

The electric conductance of potassium iodide in bromine-iodine solutions. V. PLOTNIKOV. *Z. physik. Chem.* 116, 111-18(1925).—Cond of  $\text{KI}$  in  $\text{Br}_2$  increases markedly on addn. of  $\text{I}_2$ . Sp. cond of 5% soln. of  $\text{KI}$  in 36.9% soln. of  $\text{I}_2$  in  $\text{Br}_2$  = 0.028; in  $\text{H}_2\text{O}$  = 0.034. The cond. in  $\text{Br-I}$  solns. is explained on the basis of formation of polyiodides.

S. B. ARENSON

The electrical conductance of selenium oxychloride solutions. A. P. JULIEN. *J. Am. Chem. Soc.* 47, 1799-1807(1925).—The sp. cond. of pure  $\text{SeOCl}_2$  at 25° is  $2.3 \pm 0.3 \times 10^{-4}$  mhos; the effect of common impurities on the cond is discussed. Cond of solns of  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{HgCl}_2$ ,  $\text{FeCl}_3$  and  $\text{BaCl}_2$  was detd. at various dilns. Methods for prepn of anhydrous  $\text{SeO}_2$  and its analysis for  $\text{H}_2\text{O}$  are described.

B. H. CARROLL

The physical significance of the electrolytic solution tension. J. HEYROVSKÝ. *Compt. rend.* 180, 1655-8(1925).—In establishing a thermodynamical cycle consisting of evapn, ionization and dissolv of the electrode metal a formula for the electrolytic potential is derived. Values for  $\text{Li}$ ,  $\text{Na}$ ,  $\text{K}$ ,  $\text{Rb}$ ,  $\text{Cs}$  and  $\text{Tl}$  are calcd approx and compared with the known potentials.

J. T. STERN

A method of studying electrode potentials and polarization. H. D. HOLLER. *Bur. Standards, Sci. Papers* 20, 153-66(1925).—A resistance-coupled electron-tube amplifier to operate an oscillograph is described capable of recording p. ds. at electrodes without requiring current from the electrodes under investigation. By superimposing an a. c. upon the electrode, a separately excited wattmeter could be used in measuring the p. d. due to resistance, from which the boundary resistance at the electrode could be computed. Results are given for smooth and platinized  $\text{Pt}$ ,  $\text{C}$ ,  $\text{Pb}$  and  $\text{Cu}$  in  $\text{H}_2\text{SO}_4$  soln and  $\text{Cu}$  in a  $\text{CuSO}_4$  soln.

ARTHUR GROLLMAN

**Rotatory power of cholesteric substances.** ROYER. *Compt. rend.* 180, 148-50 (1925); cf. Friedel, *C. A.* 17, 3633.—The enormous rotatory power of the cholesteric phase is due to a strong helical torsion in the substance, the rotatory power being smaller the larger the torsion. In a mixt. of amyl cyanobenzylideneaminocinnamate with cholesteryl benzoate (2.75 parts) 1) this torsion diminishes as the temp. rises from the lower transition point to the higher temp. at which the cholesteric phase passes into the nematic phase. At the same time the rotatory power increases to 7 times its initial value. The direction of the spiral torsion becomes reversed at this point, the rotatory power on either side of it for 5100 Å being +135.8 and -135.8 turns per mm. In all other cases, optical rotatory power falls with rise of temp. The cholesteric rotatory power differs in this from mol. rotation in crystals, which often rises with the temp. On the other hand, cholesteric rotatory power is quite analogous to magnetic rotation and especially with respect to the dispersion, the passage from a large value +R to an equally large -R for adjacent wave lengths being paralleled only in magnetic rotatory dispersions. The light is in both cases circularly polarized. B. C. A.

**Color and molecular geometry.** III. A graphical presentation of the theory. JAMES MOIR. *J. Chem. Soc.* 127, 967-72 (1925).—Numerous diagrams show the relative sizes and positions of the atoms in colored org. compds., the N and O atoms being placed at distances to accord with the author's theory (*C. A.* 17, 359, 18, 384) that the color is attributable to electrons in elliptical orbits around two foci which are N and O nuclei. JAMES M. BELL.

**Michelson's method for measurement of the angular distance of double stars used for the determination of the radius of small drops.** O. V. BAEYER AND ULRICH GERHARDT. *Naturwissenschaften* 13, 533 (1925).—The minimum size measured was 380  $\mu$ ; it is possible to go down to  $\frac{1}{4}$  of the wave length of the light used.

**Interaction of carbon dioxide and hydrogen in the corona due to alternating currents at high frequency.** R. W. LUNT. *Proc. Roy. Soc. (London)* 108A, 172-86 (1925).—At a frequency of  $1.5 \times 10^7$  cycles in the corona under measured voltage, amperage and power, an equil. has been attained from both sides between  $H_2$ -CO<sub>2</sub> and CO-H<sub>2</sub>O over a limited pressure range. The CO<sub>2</sub> content of the initial gas mixt. was varied from 11 to 100% and, while in the range CO<sub>2</sub> < 50% some of the monoxide was reduced (principally to CH<sub>4</sub>), in no case was HCHO or HCOOH detected. The equil. point is independent of whether the gas is circulated or confined to a small vol. and seems to be independent of the voltage applied to the gas. The latter result is similar to those of Davies on NH<sub>3</sub> (cf. *C. A.* 3, 612) and contrasts with those of Moser and Isgarishev on CO<sub>2</sub> and H<sub>2</sub> (cf. *C. A.* 4, 2769), who also found that the gases interact to form HCHO and HCOOH at the frequency 50. D. S. VILLARS.

**The use of monochromatic X-rays in the production of Laue diagrams, and the structure of mother-of-pearl (SHAXBY) 3.**

BARNOLA, JOAQUIN M.: *Autodidaxis de química práctica*. 15 experimentos al alcance de todos. 2nd ed. revised and enlarged. Barcelona. Manuel Marín. 333 pp. 8.50 ptas.

HENNIGER, KARL ANTON: *Lehrbuch der Chemie und Mineralogie*. 2 Eds., A with, B without the supplement "Elemente d. Geologie." (Ed. A) Nach systematisch method. Grundsätzen f. d. Unterricht an höh. Lehranst. edited by Martin Heidrich. 14th and 15th editions, revised. Leipzig: Teubner. 363 pp. R. M. 5.

KCSPERT, FRANZ: *Merkbüchlein aus der Chemie*. Nürnberg: C. Koch, Verlag. 56 pp.

LÖWENHARDT, EMIL: *Grundsätze der Chemie für Knaben- und Mädchenschulen gymnasialer Richtung*. Leipzig: Teubner. 45 pp. R. M. 1.

MARCOLAIN SAN JUAN, R. PEDRO: *Manual de química moderna general inorgánica y orgánica*. Sargossa: Impr. del Hospital Provincial. 479 pp. 20 ptas.

MIE, GUSTAV: *Das Problem der Materie*. Freiburg i. B.: Speyer & Kaerner. 24 pp. R. M. 1.50.

MEYER, WILHELM: *Naturlehre (Physik, Chemie und Mineralogie) für Mädchen-Mittelschulen und verwandte Lehranstalten*. 6th ed. revised. Frankfurt a. M.: Diesterweg. 280 pp. R. M. 4.

OSTWALD, WILHELM: *Die Farbenfibel*. 11 Ed. revised. Leipzig: Verlag Unesma. 47 pp. R. M. 10.

OSTWALD, WILHELM: *Die Farbschule. Eine Anleitung zur prakt. Erlerng. d. wissenschaftl. Farbenlehre*. Leipzig: Verlag Unesma. R. M. 4.

PÉREZ HERNÁNDEZ, ANGEL: *Igualdades y ecuaciones químicas*. Examen de los métodos que conducen al establecimiento de las fórmulas con que se expresan las reacciones químicas. Palma de Mallorca: Impr. Vda de G. Ordinas. 146 pp.

PUG, P. IGNACIO: *Vademecum del química*. Barcelona: Manuel Marin. 220 pp. 4 ptas.

RIO Y DE LARA, LUIS DEL: *Manual de técnica micrográfica, histoquímica, citología*. Saragossa: Impr. El Heraldo de Aragón. 252 pp. 15 ptas.

ROCASOLANO, ANTONIO DE GREGORIO and LLORENS, FELIPE LAVILLA: *Tratado de química*. 4th ed revised and enlarged. Saragossa: Talleres Gráficos Gambón. 879 pp. 28 ptas.

RODRÍGUEZ MOURELO, JOSÉ: *El mecanismo de la reacción química*. Madrid: Impr. Clásica Española. 39 pp. 2 ptas.

### 3—SUBATOMIC PHENOMENA AND RADIOCHEMISTRY

S. C. LIND

Spectroscopy and its relation to chemistry. H. DINGLE. *Chemistry & Industry* 44, 602-3, 621-7, 651-3, 674-5(1925). E. H.

The Compton effect. H. MARK. *Naturwissenschaften* 13, 494-500(1925).—A review. B. J. C. VAN DER HOEVEN

The scattering of X-rays. WM. BRAGO. *Proc. Roy. Inst. Gt Britain* 1924, (advance copy) 2 pp.—Abstract of address G. L. CLARK

The significance of spectroscopic magneton numbers. E. C. STONER. *Phil Mag.* 49, 1289-309(1925).—A brief outline is given of the Lande-Sommerfeld schemes coordinating observations on the multiplet structure of spectral lines and their Zeeman effect. The artificial and anomalous features in the attempted phys interpretations are pointed out. Simple cases are then considered. Conclusion: Electron orbits and cores are characterized by integral magnetic moments (in terms of the Bohr unit). The magnetic moment of an electron orbit is given by its azimuthal quantum no. The max. magnetic moment of a core is equal to the no. of electrons it contains in uncompleted groups. This sets the max. term multiplicity (2 greater than the core moment). Magnetic balancing in pairs of core electrons gives rise to lower multiplicities, all odd or all even for odd or even nos. of core electrons. The magnetic moments deduced spectroscopically are in agreement with those found directly in the Gerlach and Stern expts. and the core values are simply correlated with the ionic moments deduced from susceptibility measurements. The question of angular moments, and the assignment of *j* values is discussed. Finally, it is shown that a consideration of the motion of the series electron in the magnetic field of the core leads to a general qual explanation of the phys. significance of inverted terms, and interval anomalies. S. C. L.

Atomic structure of palladium and platinum black which absorb gases. ATOMI ÔAWA. *Sci Repts. Tohoku Imp Univ.* 14, 43-5(1925).—Samples of Pt black obtained (1) by electrolyzing a current of 20 milliamps. for 10 hrs. through a Pt wire anode and a 0.2 mm. Cu wire cathode in a dil. soln. of chloroplatinate at a potential of 6 v. and (2) by thermal decompn. of the alc. soln. of the chloroplatinate and the solid chloroplatinate showed several X-ray lines due to the Pt; the method of Debye and Scherrer (app. described by Yamada, *C. A.* 17, 1356) was used. Pd black obtained from an alc. soln. of PdCl<sub>2</sub> showed Pd lines. These results are contrary to those of Kirchner (cf. *C. A.* 17, 232). The linear expansion of the lattice in Pt black absorbing H<sub>2</sub>, O<sub>2</sub> and CO was 2.4, 2.9 and 2.8%, resp. The expansion of Pd black absorbing H<sub>2</sub> is the same as that of metallic Pd satd. with H<sub>2</sub> as detd. by Yamada; i. e., 2.8%. Conclusion: these gases are held in the metal as a solid soln. since the space lattice of Pt and Pd expands uniformly on absorption of the gases. D. S. VILLAS

The mass spectra of chemical elements. VI. Accelerated anode rays. F. W. ASTON. *Phil. Mag.* 49, 1191-201(1925); cf. *C. A.* 18, 1235.—This is the last of a series of papers on the isotopes of the elements as revealed by their mass spectra. The further refinements of the accelerated anode-ray method will be devoted to precision work on the whole-no. relation. The new results are for In, which showed only 1 faint line for 115; Sr, besides a very strong line for 88 has a faint one for 86 (3-4%) and by reference to I and Br lines it appears that Sr 88 is far from a whole no., which explains its low at. wt.; Ba shows a strong 133, possibly a faint 136, and 137 might also be present, but neither of the latter would account for the low at. wt. (137.37) so that possibly the 133 line is not a whole no.; La showed one line at 139; Pr showed 141

only, 139 (due to La) being absent in the purest prepn.; Nd showed 142, 144, 146 and possibly 145; Ce 140 and a faint 142. Zr showed certainly 90, 92, 94 and (96?) with intensities estd. as 10, 2, 4, (1) resp.; Cd has 6 isotopes 110, 111, 112, 113, 114, 116 with resp. intensities which show similarity in order to those of other elements like Sn, Se, Kr and possibly Hg; Te has lines of 126, 128, 130, with the 2 latter of equal intensity and double the first, which would indicate an at. wt. of at least 128 in accord with its position with respect to I, but higher than indicated by the best at. wt. detns. (127.5); Bi gave a single faint line at 209; further evidence was obtained of 3 isotopes of Si, 28, 29, 30 with an av. at. wt. indicated a little less than the International value 28.06; for Fe satisfactory evidence of 54 was obtained in the ratio about 1 to 20 of 56; Pb gives also faint evidence of complexity which could not be resolved. Of the 80 non-radioactive elements good analyses have been obtained for 56. The probabilities of further progress are as follows: Cb, Mo, Rh, Ru and Pd all have very unfavorable chem. properties for the anode-ray method but might be attacked by means of their fluorides. The same is true, but with a greater expectancy of difficulty, of the corresponding elements Ta, W, Os, Ir and Pt. Rare earth elements 62-71 are hopeful. Hf can be attacked as was Zr. Au and Tl are extremely difficult to rid of the Hg line, and Au compds. are unstable at high temps, and Au itself is very involatile. Although a knowledge of the isotopes of Th and U would be very valuable in connection with genetic problems of the 2 radioactive families of which they are the parents, attack of their mass spectra seems hopeless on account of their high at. wt. Of the other radioactive elements only Rn and Ra could be obtained in sufficient quantity, and the serious contamination of the app. did not appear to make the expt. worth while, in view of the satisfactory radioactive evidence of their simplicity. Of the 56 elements analyzed 23 were simple; 17 have 2 isotopes; 4 or 5 have 3 isotopes; and 6 have 5 or more of which 5 certainly have 6 and Xe has 7 and possibly 9.

S. C. LIND

The isotopes of lead. Mlle. BERTHE PERRETTE. *Compt. rend.* 180, 1589-91 (1925).—A comparison of 2 samples of Pb, one from Belgian pitchblende with an at. wt. 206.14 and the other ordinary Pb with an at. wt. 207.20 gave the following results, resp.  $d$ , 11.278, 11.336, at. vol. 18.2774, 18.2776. A comparison of the spectra gave the following results:

$\lambda$	$d\lambda$ (U Pb — Ordinary Pb)
4058	0.0076
3740	0.0070
3684	0.0073
3640	0.0072
2573	0.0068

MARIE FARNSWORTH

The origin of radioactivity. E. BRINER. *Compt. rend.* 180, 1586-9 (1925).—The exothermic decompn. of Ra can be made compatible with the exothermic synthesis of its elements from their primal constituents (protons and electrons). The disintegration of Ra,  $Ra \rightarrow 5He + Pb + Q$ , does not imply that the formation of the atoms of Ra starting with its primal constituents is endothermic; it may be largely exothermic but less than that of the system  $5He + Pb$ . Analogous cases are the decompn. of  $2O_2 \rightarrow 3O_2$  and the H particles liberated in the decompn. of Al and P, which have more energy than the  $\alpha$ -particles causing the disintegration.

MARIE FARNSWORTH

The long-range particles emitted by the active deposit of thorium. NUBUO YANADA. *Compt. rend.* 180, 1591-4 (1925).—The active deposit of Th emits 2.9  $\alpha$ -particles of 11.5-cm. range for each 10,000  $\alpha$ -particles of 9.6-cm. range. The particles of 15 and 18.4-cm. range are probably H-particles, emitted by the bombardment of  $\alpha$ -particles.

MARIE FARNSWORTH

The adsorption and the reversibility of the adsorption of polonium by various materials. J. H. BRENNEN. *Ann. chim.* 3, 390-418 (1925); cf. C. A. 18, 3001.—In the adsorption of Po by different colloids such as Ag, Fe(OH)<sub>3</sub>, Al(OH)<sub>3</sub>, and SiO<sub>2</sub>, the same equl. is attained in about  $\frac{1}{2}$  hr., whether one adds the Po to the colloid or to the pptd. colloid. In the adsorption of Po by insol. salts, not attacked by HCl or CH<sub>3</sub>COOH (AgCl, PbSO<sub>4</sub>, BaSO<sub>4</sub>, and SrSO<sub>4</sub>), the adsorption is dependent on the H-ion concn, increasing as the concn. of acid decreases and becoming max. in a neutral soln. There is an equl. between the carrying down of the Po and its removal under identical conditions of acidity but the adsorption of Po is rapid and its removal slow. The Freundlich law of adsorption was found applicable for the adsorption of Po of activities 2.24 and 27 E. S. U.

MARIE FARNSWORTH

Electrical properties of neon, hydrogen and nitrogen. S. P. McCALLUM AND

C. M. FOCKEN *Phil Mag* 49, 1309-20(1925).—The results are given of measurements of the current voltage relation in the discharge in these gases under the same conditions as recently reported for He (*C. A.* 18, 1946). S. C. L.

The behavior of hydrogen in the discharge due to alternating electric fields of high frequency. R. W. LUNT *Phil Mag* 49, 1238-49(1925).—An analysis of the Sienert's ozonizer is put forward which affords a ready detn of the voltage gradient and of the current carried by the ions in the gas. An attempt has been made to det the approx mean intensity of ionization in H under any given elec conditions by a simple equation relating the cond current in the ionized gas to the known motions of ions and electrons in H and to the impressed elec force. The 2 quantities, the impressed elec force and the resulting mean fractional intensity of ionization in H, have been detd at the frequency  $1.5 \times 10^7$  over the pressure range 10 to 50 cm and over the available range of elec conditions. The concept of "equiv. temp" is discussed with reference to the discharge in H. S. C. L.

The present status of the theory of the glow discharge. II. R. HOLM *Physik. Z.* 26, 412-20(1925), cf *C. A.* 19, 436. F. H.

The quadratic Zeeman effect. A. LANDÉ *Z Physik* 30, 329-40(1924).—A theory for moderate magnetic fields is developed by means of which the unsymmetrical (proportional to field strength) disturbances of Zeeman types at the beginning as well as at practically complete Paschen-Back effect can be predicted. The calcd results are compared with observations of Back on the Na-doublet 3303 Å U, and the Mg triplet 5167, 5172, 5183 Å U., the fields being 32,988 and 38,900 gauss, resp. The excellence of the agreement is regarded as new confirmation for the law of permanence of the g-sums, and also as an indication that the mechanics of the model is in many ways a picture of the reality. W. F. MCGOWAN

Electrical conduction, number of charges, mobility and thermal ionization in flame gases. ERICH MARX *Ann Physik* 76, 737-84(1925).—A paper of great importance in the theory of flame conduction, in which M. points out that his previous statements that the Lenard theory of ionization by impact of metal atoms in flames was incorrect in view of the fact that Ohm's law of cond, in flames and Arrhenius' law of the proportionality between cond and the square roots of the concn of salt atoms coexist, must be modified by the new understanding of temp ionization introduced by the theory of Saha. This theory indicates that both the temp ionization of the Lenard type and as the photoelec. ionization which Marx postulated, in place of the Lenard ionization, operate together in equil. He indicates that a sepn of the 2 effects in the flames is impossible since the temp detts the equil of both processes, so that the degree of dissociation depends only on the ionization potentials, and not on the mechanism which happens to liberate the particles. The paper contains a detailed discussion of the phenomenon of ionization in flames in the light of the new Saha theory. M. is led to conclusions of which some of the shorter and more important ones follow. In flame ion-mobility measurements one detts a quantity  $\beta K$  which is not a true mobility but is termed the "displacement" of the ion. It is really the product of the mobility  $K$  of the ion by the fraction  $\beta$  of the time during which it is charged ( $\beta$  is its charge const.). The method of opposing fields is only valid where there is a rapid change of charge, and fails when the fields become so weak that they are small compared to the forces of diffusion. All previous formulas deduced for the charge const  $\beta$  (Ladungs zahl) must be abandoned in view of the changes of mass as well as charge occurring. A new relation connecting at, wt, concn, and recombination is deduced which gives directly the Arrhenius concn. law, the square root law of the mobilities of Marx, the Smithells-Wilson-Dawson characteristic relationship, and the Zachmann rule for the cond. The charge const  $\beta$ , which is the fraction of the time that the ion is charged, is proportional to the inverse square root of the at wt and concn, while the degree of dissociation is directly proportional to the square root of these quantities. The calcn of the degree of dissociation of the vapor and metal is impossible on the basis of the Saha formula as the sp heats of the vapors are not known. The relation between the at wt and dissociation, above mentioned, leads to subsidiary equations which enable the dissociation const and the degree of dissociation for the alk vapor, for the metal to atom ion and electron, as well as the sp heat to be detd. It is indicated that the previous use of the Saha equation by Noyes and Wilson is hardly capable of giving a first approximation to the correct result. The quantities above once detd, lead with an exptl knowledge of the displacements and the cond, to a complete quant. understanding of the consts. of flame cond. From the measurements of pure flames it is found that no change of charge but merely changes in mass of the carriers occur. Further conclusions can then be drawn concerning the way in which different carriers change their masses

in relation to the flame gases, the atoms of Cs, Na and K, and Li showing different tendencies in this direction L. B. LOEB

**Abnormal low-voltage arcs in mercury vapor, argon, and helium.** R. BÄR. *Z. Physik* 31, 430-8(1925); cf. Eckart and Compton, *C. A.* 18, 3525; Bär, Laue and Meyer, *C. A.* 18, 1429.—The low-voltage arcs obtained by a potential difference of a few v in Ne, A and Hg vapor are not caused merely by oscillations, but correspond with true abnormal arcs. In He such an oscillation free, low voltage arc can only be obtained after the strongest heating of a filament, and a potential difference of 16.5 v (which is not far from the excitation potential of He) is required. The av. voltage required for a He arc caused by oscillations is 8. B. C. A.

**The theory of collisions between atoms and electrically charged particles.** E. FERMI. *Z. Physik* 29, 315-27(1924).—The elec. field of a charged particle which passes close to an atom is harmonically analyzed and compared with the elec. field of light with a suitable frequency distribution. It is assumed that the probability that the atom is excited or ionized by the passing particle is equal to the probability of excitation or ionization by the equiv. light rays. These assumptions are applied to excitation by electron impact and to the ionizing effect and range of  $\alpha$  rays. A. E. STEARN

**Influence of ionic diffusion on almost saturated currents.** GEO. JAFFÉ. *Ann Physik* 75, 391-402(1924).—A theoretical discussion of the effect of the diffusion of gaseous ions upon the current voltage curves of condensers, near the satn. point. Expressions are developed for the characteristics of plate, cylindrical and spherical condensers. B. C. A.

**Ionization of iodine vapor by ultra-violet light.** W. WEST AND E. B. LUDLAM. *Proc. Roy. Soc. Edinburgh* 45, 34-41(1925).—By using a powerful spark between carefully cleaned Al terminals (a 10,000-v transformer with 10 amps in primary), a mm or so outside of a fluorite window 13 mm thick the authors found an ionization current of  $10^{-12}$  amp inside an ionization chamber through which a mixt. of illuminated I vapor and pure  $N_2$  gas was flowing. The pressure of the  $N_2$  was between 10 and 1 mm and the I vapor had a pressure of 0.13 mm. The ionization was the same whether the collecting electrode was positive or negative. It did not appear when the I was absent from the stream, nor when the spark was removed 1 cm. from the window in the air. When the electrodes became coated with oxide it ceased, to reappear again when they were cleaned. The ionization p. d. estd. for the I, mol. lies between equiv. wave lengths of 1230 and 1310 Å. U. They estd. that their fluorite just let through the lower wave length. The arc was especially strong in lines about 1800 Å. U. It is possible that some of the ionization came from the action of the light of 1800 Å. U. on the fluorescent  $I_2$  mol's. Conclusion: light of wave lengths below 1800 Å. U. is able to ionize mol. I vapor. L. B. LOEB

**The ionization of potassium vapor by visible light.** ALBERT ARNULF. *Compt. rend.* 180, 1259-62(1925).—A. uses an evacuated bulb contg. an incandescent filament and a plate electrode with a small deposit of K in its bulb. The filament is heated to incandescence and a current registered by a microammeter is produced on applying a potential between the plate and the electrode. If a beam of light is passed through the cell, which contains K vapor as a result of the heat of the filament, the current suffers a sudden increase of from 14 to 20%. A. attributes this to a partial neutralization of the space charge effect by the positive ions produced by the ionization of the K vapor by the external source of light. Thus he claims to have demonstrated the ionization of K vapor by visible light. L. B. LOEB

**Magnetic properties of atoms and molecules.** B. H. WILSDON. *Phil. Mag.* 49, 1145-64(1925).—In 2 previous papers (*C. A.* 19, 1814, 2580) heats of formation have been calcd. from at. structure. In the present paper the magnetic properties of some compds. and elements are calcd. With polar compds. the magnetic properties are calcd. for some of the F, Cl, Br and I salts of Li, Na, K, Mg, Ca, Sr, Ba, Zn, Hg and Ag with good agreement with the exptl. values except for the F compd., where agreement was not expected. The calcn. was for the elements Ag, Cu, Zn, Ca, Hg, N, B, P, As, Sb, C and S also with fair agreement. S. C. L.

**Constancy of total photo-current from sodium with temperature change  $20^\circ$  to  $-190^\circ$ .** ROBT. C. BURT. *Phil. Mag.* 49, 1168-76(1925).—An examn. of the influence of temp. on the photoelec. emission from Na. The Na was purified by electrolyzing through a soda-glass W-filament lamp immersed in a bath of molten  $NaNO_3$ . The vacuum in cells sealed off from the pump was not maintained sufficiently to keep the Na surface clean, even with charcoal-liquid air side tubes. It was necessary to keep the pump in operation. The total photoelec. current of Na is const. within a few % between  $20^\circ$  and  $-190^\circ$  if the Na surface is sufficiently pure. Slightly contaminated,

the surface may be much more sensitive at low than at room temp.; but if slightly more contaminated by some unknown vapor it may be several times less sensitive at the low temp.

S. C. L.

The use of monochromatic X-rays in the production of Laue diagrams, and the structure of mother-of-pearl. J. H. SHAXBY. *Phil. Mag.* 49, 1201-6(1925).—See C. A. 19, 914.

S. C. L.

The absorption of superposed X-radiations. W. H. WATSON. *Proc. Roy. Soc. Edinburgh* 45, 48-58(1925).—From certain peculiar changes in the mass absorption coeffs. of Al when illuminated with heterogeneous X-rays in a study of the J radiation effect by Barkla, and from results obtained by C. T. R. Wilson in cloud expansion measurements in  $N_2$ , where paired electrons of different energies were liberated from the primary X ray beam, W. suspected that the mass absorption coeff. of Al for X rays of a given wave length might be altered by the superposition of a second radiation on the absorber at the same time. Under rather difficult exptl. conditions the expt. was performed with results of a predominatingly negative character. Where from the J radiation phenomenon a change of 13% might have been looked for an occasional effect of about 4% was observed in 1 series. Conclusion: The effect of the superposed radiations on electronic radiations observed by Wilson does not appreciably affect the absorption. Wilson's phenomenon does not take place on the Al in these expts. L. B. L.

Applications of the correspondence principle to the theory of line-intensities in band spectra. R. H. FOWLER. *Phil. Mag.* 49, 1272-88(1925).—A general summary of the Correspondence Principle and its "refined" applications is given, with special reference to band spectra. It is shown that the intensities of the lines in a single band must be expected to obey summation rules similar to those first recognized by Ornstein, Burger and Dorgelo in at. spectra. Precise formulas for the relative intensities are given in terms of the wts. for the lines of any band without a zero branch. With the help of mol. models the theory can probably be extended to include bands with zero branches. So far as the present rather meager exptl. data extend, the theory seems to be in agreement with fact. It promises, when better exptl. data are available, to provide direct evidence as to the wts. of the states of a rotating mol. and thus fill up an important gap in existing theory. It therefore suggests lines for fruitful exptl. work.

S. C. L.

The polarization of the light scattered by organic vapors. A. S. GANESAN. *Phil. Mag.* 49, 1216-22(1925).—In the paraffin series of compds. as one passes from pentane to octane, the mols. become longer, and if one associates optical anisotropy with anisotropy of shape, one might expect an increasing optical anisotropy as one goes up the series. But from the values given above, it is clear that there is no such increase in the depolarization; if anything, there is a tendency for an actual decrease in the value. Another interesting fact is that whenever there is a "double bond" in the structure of the mol. there is a high value for the "factor of depolarization." This is to be seen with the unsatd. hydrocarbon amylene, which has a value nearly twice that for the paraffin series, and also with allyl alc., where the depolarization is much greater than that for the monohydric alcs. The iso compds. show a smaller optical anisotropy than the normal ones. The benzene series affords a very interesting study. The 3 homologs benzene, toluene, and xylene show the same degree of imperfection, namely 6.5%. This may be explained as due to the predominating influence of the closed chain of the 6 C atoms, the H or its substitution by an alkyl radical exerting little or no influence on the optical anisotropy of the mol. The Me compds. always show a greater imperfection of polarization than the Et compds. This is to be seen not only with the formates, acetates, and alcs. but also with the ketones, where dimethyl ketone contg. 2 Me radicals shows a greater value for  $\rho$  than the other 2 compds. As is to be expected, the more sym. mol.  $CCl_4$  shows a smaller value for  $\rho$  than  $CHCl_3$ . Expts are in progress to investigate the effect of successive replacements of H by Cl in  $CH_4$ . S. C. L.

Emission band spectra of aromatic compounds. II. Their origin. Jos. K. MARSH. *Phil. Mag.* 49, 1206-16(1925).—From a consideration of a parallel between the infra-red band intervals of ethylene and the ultra-violet band intervals of benzene, naphthalene, and anthracene, the bands exhibited by these substances are considered to originate in a  $C=C$  bond. Similarly the band intervals of type (2) of the preceding paper (C. A. 19, 2452) are shown to originate in a  $CH$  bond. Benzene also shows vibrations having this origin, and the spectrum is accounted for as a combination of  $C=C$  and  $CH$  vibrations. It is considered most probable that the "blue band" type of spectrum originates from a  $C=O$  bond and evidence on this point is brought forward. A view of the benzene mol. is taken accounting for the fact that the bands originating from the 2 C atoms of the  $C=C$  bonds show evidence of their being in a

state of mutual rotation, while the CH groups appear to have a rotation frequency of which their vibration frequency is an exact multiple. This is necessitated if the symmetry of the mol. is to be preserved. S. C. L.

**The broadening of lines in arc spectra and the Stark effect.** H. LOWERY, *Phil. Mag.* 49, 1176-83 (1925).—Notes on the work of Kimura and Nakamura (*Japan J. Phys.* 2, 61 (1923)) on the broadening of the lines of the arc spectra of Cu, Ag, Au, Mg, Ca, Cr and Ni, in which attention is drawn to the similarity of the broadening of the lines produced by (1) the interrupted arc spectra of Cu, Ag, Au, Ni and Mg, and (2) the heavy current arc of K and Na. The broadening is such as would be expected from observations on the Stark effect. In interpreting the broadening of the lines obtained by Duffield (*C. A.* 2, 363, 5, 238, 9, 1872) in expts. on the effect of pressure on arc spectra, it is necessary to take into account the effects due to the heavy currents employed and the necessity for repeatedly striking the arc. S. C. L.

**Arc spectrum regularities for ruthenium.** W. F. MEGGERS AND OTTO LAPORTE, *Science* 61, 635-6 (1925).—Photographs of the spectrum emitted by a condensed spark under water showed 85 distinct absorption lines between 2255 and 4709 Å. From these the lowest term of the Ru arc spectrum is recognized as being a 5-fold term with the septus, 392.2, 621.7, 900.9, 1190.8  $\text{cm}^{-1}$  and the inner quantum nos. 0, 1, 2, 3, 4, which in analogy with Fe may be regarded as a quintet D-term. This term combines with 46 or more higher levels, thus accounting for a majority of the strong Ru lines. The lines 3436.74 and 3498.95 Å. occur in a  $^4D - ^4F$  combination. W. F. M.

**A simple spectroscopic device for work in the visible and ultra-violet spectrum.** W. STEUBING, *Physik. Z.* 26, 329-31 (1925).—The prepn. is described of a plate coated with fluorescent material, uranyl fluoride-ammonium fluoride, to be used for visual examn. of dispersion, focus and brightness of spectrographs throughout the visible and ultra-violet spectrum to 1850 Å. U. W. F. MEGGERS

**The band spectra of crystals and complex gases.** H. KÄHLER, *Proc. Nat. Acad. Sci.* 11, 286-9 (1925).—The luminescent spectra of the uranyl salt crystals show high- and low-frequency branches of bands which can be expressed by an equation of the well-known band spectral type. The spectral changes for uranyl salts in soln. are interpreted as the effect of coupling upon the characteristic localized vibrations, due to the solvent mols. With several org. vapors the spectra must be expressed by means of multiple linear terms. They appear to be more general applications of simultaneous combination transitions. W. F. MEGGERS

**The system of band spectra.** R. MECKE, *Z. Physik* 28, 261-77 (1924); cf. *C. A.* 18, 1613.—The second positive group of N bands leads to a quintet system of spectral terms, while the spark spectrum of the N<sub>2</sub> mol., the negative bands, in agreement with the displacement law, to a doublet system. In general the same points of view which have made it possible to analyze the line spectra of atoms apply also to the classification of the band spectra of mols. In either case the spectra are described by 3 quantum nos., *K*, *J* and *R* and certain selection rules governing the combinations of spectral terms. A band system is thus equiv. to an entire multiplet system characterized by the (multiplicity) no. *R*. The regular alternation of even and odd multiplets in the periodic system of the elements is also characteristic of band spectra so far as the data go; the displacement law appears to be valid for band spectra, and further, a transition from the at. to the corresponding mol. spectrum involves a change in the multiplicity of the terms. W. F. MEGGERS

**Quartet system multiplets in the arc spectrum of yttrium.** W. F. MEGGERS AND B. E. MOORE, *J. Wash. Acad. Sci.* 15, 207-10 (1925).—New measurements of magnetic resolutions of Yt arc lines revealed the quartet system of spectral terms. The prominent terms are strictly analogous to those in Sc; a low  $^4F$  term combining with higher  $^6G$ ,  $^6F$  and  $^6D$  terms gives 3 multiplets of strong lines in the visible spectrum. Tables are given for the relative terms, the multiplets, and the Zeeman effects of the individual lines. Satisfactory agreement between the observed and theoretical patterns is noted. W. F. MEGGERS

**Quantitative study on the ultra-violet absorption of aqueous solutions of potassium permanganate.** EMILIO VIERERI, *Gazz. chim. ital.* 55, 127-35 (1925).—The absorption spectrum of the permanganates has been much studied; it is a characteristic spectrum of fine bands that is not generally found in inorg. compds. except in the salts of the rare earths. But 2 authors have previously observed the ultra-violet absorption of  $\text{KMnO}_4$ . The results obtained, of which the details are given, showed that 2 absorption bands for  $\text{KMnO}_4$  exist in the ultra-violet. The first of these shows 7 and perhaps more fine absorption bands analogous to the 8 of the visible band. The order of succession according to their mol. coeffs. of absorption for the fine bands in the ultra-violet

is the same as that for the visible fine bands. The coeff. maxima are about the same for these 2 characteristic bands. Of these 2 bands also each has associated with it in the less refrangible part another band that does not appear to belong to the system of fine bands. The differences between the centers of frequency of 2 adjacent fine bands in the ultra-violet and in the visible range are nearly equal. These facts and those obtained by Henri with aromatic compds. indicate the probable existence of a band in the infra red at the frequency  $V = \pm 22 I$ . E. J. WITZEMANN

Fine structure of the helium line 5876 Å. U. R. BRUNETTI. *Atti accad. Lincei* [v], 33, n, 413-5 (1924).—The  $D_2$  He line appears to be undecomposable and endowed with only a single satellite. Both retain their sep. structures in even intense magnetic fields and are, therefore, not lines of a multiple series in the ordinary sense of the term. The origin of the structure of the He line 5876 Å. U. is thus still unexplained. B. C. A.

Radiation emission of molten aluminium. M. MOELLER AND H. MEYERHOFF. *Giesserei-Ztg* 21, 444-6 (1924).—The emissive power of a surface of molten Al exposed to the air increases from 0.12 at 700° to 0.17 at 1000°. The temps. as measured by the Holborn-Kurlbaum radiation pyrometer show therefore great deviations from the true temp.; these have been measured and a graph has been constructed, but still considerable errors are introduced by the formation and thickening of the oxide layer. B. C. A.

The spectra of doubly and trebly ionized phosphorus ( $P_{III}$  and  $P_{IV}$ ). M. O. SALTSMARK. *Proc. Roy. Soc. (London)* 108A, 332-43 (1925).—Observations were made on the spectrum of P under various conditions from 1250 to 7113 Å. U., the source being a condensed discharge through the vapor of yellow P in a tube with Al electrodes, arranged so that H could be introduced. In order to classify the lines and assign them to the various stages of ionization of the P atom, photographs were taken, the discharge through the vapor being varied either by adjusting the pressure of the residual H or by the insertion of self-induction in the circuit. In the former case, when the pressure of H was sufficiently low, intense discharge took place mainly through the P vapor; a great many P lines then appeared, some of great intensity. Ten doublets are ascribed to the spectrum of doubly ionized P, and a singlet S term, a doublet P and a doublet D term are ealed on the assumption that the series const. is 9 R. In accordance with the spectroscopic displacement law the spectrum  $P_{III}$  should be characterized by doublets but that due to  $P_{IV}$  should contain triplets. Three triplets were actually identified as belonging to  $P_{IV}$  on account of the values of their sepns and their positions; they lie upon the curves of wave no. of series line and at. no. for the group Mg, Al, Si, S, P, Fe. Approx. term values were ealed with 16 R as the Rydberg series const. It has been observed that for 3 groups of elements, each having its own characteristic electron structure, the sharp terms are greater than the diffuse terms with the same Rydberg no. for the neutral and singly ionized element, but for higher stages of ionization the diffuse terms are greater than the sharp. W. F. MEGGERS

Further spectra associated with carbon. R. C. JOHNSON. *Proc. Roy. Soc. (London)* 108A, 343-55 (1925).—In a previous paper (cf. C. A. 17, 2833), Merton and Johnson described the action of He in isolating and modifying spectra associated with C. Uncondensed discharge through tubes contg. a trace of CO in some 20 to 30 mm. He produced a band spectrum like that in comet tails, while a mild condensed discharge yielded spectra of He and a new line spectrum attributed to C. Since both of these were investigated only in the visible region, the present paper records observations of these spectra in the ultra-violet. Some new lines were observed but a preliminary search has revealed no triplets such as might be expected for neutral C on the basis of the displacement law. The comet-tail bands were extended to 3428 Å. U. and the series formulas recalcd. A new band spectrum apparently associated with the comet tail bands was measured. Advantage was taken of the unexpected strong development of the negative C bands to photograph this spectrum. About 40 band heads are measured (3153 to 2413 Å. U.) and arranged in series. Diatomic mols. are believed to be responsible for these bands. W. F. MEGGERS

An absorption line of the iodine atom. CHR. FUCHTBAUER, F. WAIBEL AND L. HOLM. *Z. Physik* 29, 367-71 (1924).—A quartz tube, 70 mm. long, of I vapor was used together with a Zn spark as source and quartz spectrograph with Schumann plates to photograph the spectrum to 1830 Å. U. The tube was heated in an elec. furnace; it had a side tube immersed in water so that the pressure of I might be varied by the water temp. (50° to 60°) independently of the temp. of the furnace (1050°). The first absorption line due to the I atom is at 2062 Å. U., which corresponds to an excitation potential of 5.99 v. At the high temp. required for dissociating the  $I_2$  mols. an absorption spectrum due to  $O_2$  is strongly developed and the observations of the fine lines due to I are difficult. Attempts to increase the width of the line 2062 Å. U. by increasing the v. p. were futile.

because the absorption of the  $I_2$  mol became too intense. The necessary line width was obtained by adding A of 3 atm. pressure. W. F. MEGGERS

The spectra of the metals of the aluminium sub-group. K. RANGADHAMA RAO. *Proc. Phys. Soc. London* 37, 259-64(1925).—The absorption of Tl vapor from 2400 to 2000 A. U. and that of In vapor from 6000 to 2000 A. U. was studied by means of a steel absorption tube with quartz windows, a quartz spectrograph, and high-frequency Al spark under water which furnished the continuous spectrum. The tube was heated in a charcoal furnace, temps. of the order of  $1500^\circ$  being easily obtained. In addn. to lines given in another paper (cf. C. A. 18, 3142) 10 more series lines of Tl and 3 non-series lines were found in absorption. Twenty-one In lines (4501 to 2179 A. U.) were found in absorption and 3 non-series lines. The first members of the series,  $1s_2 - m8'$ , of both Tl and In exhibit asymmetrical absorption. In both cases there appear at high temps. and on the short-wave side of  $1s_2 - 2s'$  channelled spectra consisting of asymmetrical bands degraded towards the red. None of the lines of the principal series appears in absorption even at the highest temps. The absorption of In is very feeble when compared with Tl though the m. and b. ps. are lower for the former. This difference may be due to the difference in the valencies, m being strongly trivalent while Tl is predominantly univalent. W. F. MEGGERS

The measurement of absorption in the ultra-violet spectrum. G. M. POOL. Z. *Physik* 29, 311-4(1924).—A method of photographic spectrophotometry especially adapted for measurements in the ultra-violet is described. All optical parts are of quartz; a monochromator is introduced to reduce scattered light; a rotating variable sector is used to change the light intensity. Application of the method is illustrated by measurements of  $\epsilon$ , the mol. absorption coeff., for acetone and for  $MgCl_2$ ,  $CaCl_2$ ,  $SrCl_2$  and  $BaCl_2$ , the ultra-violet limit being at 2400 A. U. W. F. MEGGERS

The experimental control of electrically broadened spectral lines. M. C. JOHNSON. *Proc. Phys. Soc. London* 37, 219-58(1925).—Previous researches in the control of broadened spectral lines have either been confined to the variation of gas pressure in the discharge tube, or, when elec. conditions have been studied, they have been confined to the variation of the external circuit: work by this method has been reported concerning broadening of Balmer lines over a range of 10 to 50 A. U. The present expts. are an attempt further to disentangle conditions (a) by using a range of 0.3 to 1.0 A. U., in which changes hidden in the wider range might be detected, and (b) by using other means of control in addn. to the external circuit; this latter is important in view of the suggestion that capacity and inductance control of broadening at apparently const. pressure act by a secondary effect on temp. and pressure. H tubes of the usual Plucker type were excited by a 5-inch spark coil worked on 20 v. with a Hg-motor break, and the spectrum was analyzed by a Hilger const.-deviation spectroscope and 20-plate echelon. If the broadening of the spectral lines with current density is considered to be a Stark effect, concn. of ions is the obvious controlling factor; recombination of ions on this hypothesis may explain the way broadening varies with inductance or with capacity according to these expts. This view is further tested by controlling the broadening without altering the current in the tube or the period of the discharge; for this a range of widening over which rectified and unrectified discharges show lines differing in width is provided by a magnetic field. The several effects involved in this expt. are accounted for on the theory that line width depends on the number of charges which surround an emitting particle. A thermionic method is also employed for varying the line width by drawing into the discharge, ions in addn. to those produced by collision; lighting a filament in a specially constructed discharge tube facilitated recombination of ions and decreased the line width. W. F. MEGGERS

Luminous vapor from the mercury arc and the progressive changes in its spectrum. LORD RAYLEIGH. *Proc. Roy. Soc. (London)* 108A, 262-79(1925).—An investigation of the luminous stream of vapor which is observed when Hg distills away from the arc *in vacuo*. The spectrum lines (1850 A. U. to red) of the arc forming known spectrum series are for the most part strongly developed in the vapor stream. An exception to this is the line 1850,  $1S-2P$ , which is strong in the arc but inconspicuous in the distd. vapor. The arc lines not hitherto classified into series are faint or absent in the vapor stream. The higher members of the various series appear in greater relative intensity in the distd. vapor than in the arc. In some cases the intensity of these higher members is even absolutely greater than in the arc. As the luminous stream passes on, the character of its light changes, the higher members of the various series lose intensity relative to the earlier members, so that there is a relapse to and beyond the intensity distribution in the arc. The line 2537,  $1S-2p_2$  steadily gains in relative intensity as the vapor matures, ultimately becoming the strongest in the spectrum. The continuous

spectrum of Hg, not noticeable when the vapor first emerges, becomes more and more conspicuous as the vapor matures. In the limit the spectrum tends to consist simply of the line 2537 and the continuous spectrum. The continuous spectrum, whether produced in this way or directly by elec. discharge, stops abruptly on the more refrangible side at 2537. On the less refrangible side it extends into the red. It is found that if the vapor is passed through a metal tube maintained at a negative potential, the luminosity of the line spectrum in general tapers down to a sharp point, beyond which it disappears entirely. The line 2537, behaves differently. Much of its light is subject to the action of the elec. field, and tapers down to a point, which, however, is beyond the place where the other lines are extinguished. A residuum of the light of 2537 is of a different origin, and does not admit of extinction. It passes on unaffected by the field. The light of the band spectrum also passes on. When 2537 and the band spectrum have thus been isolated, their intensity at a fixed place in the tube is diminished if the place where the elec. extinction of the line spectrum occurs is moved upstream of its former position. The bearing of these facts is discussed, but many of them appear very difficult to bring into line with accepted views as to the origin of spectra.

W. F. MEGGERS

**Luminescence in the Ingleside calcites affected by acids.** WM. P. HEADDEN *Am. J. Sci.* 8, 503-17(1924).—Some rather peculiar results were obtained on insulating samples of calcites obtained at different places at or near the Ingleside region in Colorado. The complexities of this question, compn. of sunlight, the effects of atm. conditions, variation in individual samples, lack of permanency in these properties themselves, and their susceptibility to radiation, and even to disturbances set up by the action of acid on the calcite, are extremely perplexing.

E. P. WIEGGMAN

**The chemical action of light.** A. BOUTARIC *La nature* 53, 1, 115-9(1925).—A general description of the effect of light in inducing chem. reactions, with particular reference to the work of Berthelot (cf. *C. A.* 12, 2282).

C. C. DAVIS

**Criticism of the work of W. T. Anderson, Jr., the photolysis of potassium nitrate solutions.** E. WARBURG *Z. Physik* 29, 344(1924).—Refutation of Anderson's criticism (*C. A.* 18, 1614) of his own work on the same problem (*C. A.* 14, 1930).

A. E. STEARN

**A note on the photoactivation of chlorine.** WILFRID TAYLOR, *Phil. Mag.* 49, 1165-8(1925).—T. has used the Bunsen and Roscoe actinometer to det. the relative activation of the  $H_2-Cl_2$  mixt. for different spectral band regions. A pointolite arc was employed with a water cell and light filter. Correction was made by means of a thermopile for the quantities of radiant energy transmitted by each filter. The results are:

Filter	Reaction velocity	Range of wave band (A U)	Relative light intensity	Corrected activating power
Violet	100	4300-4800	7	100
Blue	27	4550-5000	11	17
Blue green	14	4780-5370	13	8
Green	0	5050-5570	15	0

It is concluded that it is the general absorption of  $Cl_2$  itself in the band extending from 4900 A U, that is, the activation region and not the Ribaud fine structure bands. Activation seems, therefore, in this case to be concomitant with the non quantification of the vibratory motions.

S. C. L.

**The variation of the temperature coefficients of photochemical reactions with the frequency.** M. PADOA *Gazz. chim. ital.* 55, 87-92(1925).—In previous papers P. et al. (*C. A.* 9, 3066, 10, 1466; 11, 796, 1356, 1796) found that the temp. coeffs. of the photochem. reactions examd. are variable with the frequency and decrease with increasing wave length. At that time it was said that the greater frequency corresponds to higher temps. and that the mols. and atoms absorbing the light of shorter wave length are colder. This same concept can be expressed in modern chemico-kinetic terms (Pratolongo, *C. A.* 15, 2765) and this is discussed in some detail. In the cases known up till now the variation of the temp. coeffs. is in the sense of an increase with a diminution of the frequency and is interpreted as a variation of the affinity between atoms and electrons according to the frequency of the light absorbed in the sense that in the atoms of mols. that have absorbed light of less frequency such a sepn. or dissociation as occurs requires a greater outlay of energy. In the expts. described in this paper on the photochemical oxidation of HI the temp. coeffs. contrary to the general rule, diminish with diminution of the frequency. This may be interpreted: (a) by admitting that in this case the affinity between atoms and electrons, or the energy of activation, may be

greater for the greater frequency; (b) or more probably, on the contrary, that it may always be greater for the smaller frequency and that such abnormal variations of the temp. coeffs denote a transformation of frequency on the part of the body that absorbs the light. E. J. WITZEMANN

#### 4—ELECTROCHEMISTRY

COLIN G. FINK

**Calcium carbide—notes on its production and properties.** C. COULSON SMITH. *Chem. Trade J* 76, 723-4(1925) —When coke is used in  $\text{CaC}_2$  manuf., the  $\text{Fe}_2\text{O}_3$  present, about 2%, combines with the Si to form ferrosilicon. The limestone used should contain at least 97%  $\text{CaCO}_3$ , no more than 1%  $\text{SiO}_2$ , 0.5%  $\text{MgO}$ , or 0.01% P. The impurities of carbide are classed as those decomposed by water, and those not so decomposed. When C is in excess blue crystals of carborundum are formed, while if Ca is in excess  $\text{Ca}_2\text{Si}$  is formed. A good carbide may be distinguished from an inferior one by breaking a piece from a newly opened drum, and noting the color of the fracture. When the color is gray, the piece fairly difficult to break and the fracture shows a crystal structure with bluish streaks, then the carbide will give a high yield of  $\text{C}_2\text{H}_2$  and the gas will have a low P content. If the carbide has a reddish color, is easily broken, and the fracture is similar to a piece of sandstone, the gas yield from it will be low and the gas impurities high. Improved methods of sampling and analysis are suggested. W. H. BOYNTON

**Calcium carbide and cyanamide.** JEAN GALL. *J. four. elec.* 34, 139-41(1925). —A review. C. G. F.

**Electrodeposition of copper-nickel alloys.** H. D. HINELINE AND W. B. COOLEY. *Trans. Am. Electrochem. Soc.* 48 (preprint)(1925) —Expts were conducted in the simultaneous deposition of Cu and Ni from a bath contg. fairly high concns. of the mixed double cyanides, 50 to 150 g. per l. It was found possible to deposit coatings having a wide range of compn. from almost a full Cu red to a white alloy. Satisfactory anode corrosion was obtained upon adding from 5 to 40 g. per l. of KCl. The bath must be worked at a low temp., preferably below 18°. Very high current densities, as high as 25 amp. per sq. dm., are possible. An unusual cathodic cleansing of greasy, varnished, or rusty work was observed, due probably to H. The resulting deposit of Cu + Ni was extremely ductile, suggesting an unusual state of the metal. Microscopic examn. of the deposit was not made. C. G. F.

**Peroxidized lead anodes.** Preliminary note. GRINO BOZZA AND MARCO BEROZZI. *Giorn. chim. ind. applicata* 6, 571-5(1924) —Preliminary tests upon Pb anodes in  $\text{H}_2\text{SO}_4$  solns. contg. varying amts. of Cl, with diverse current densities showed that the critical concn. of Cl for largest yield of  $\text{PbO}_2$  was about 0.28 g. per l. The critical c. d., below which the attack upon the anodes was most pronounced, was about 2 amp. per dm.<sup>2</sup>. The best current yields were about 60%. ROBERT S. POSMONTIER

**Investigation of Leclanché cell for pocket flashlights.** MARTIN GRUHL. *Z. Elektrochem.* 31, 214-49(1925) —A study is made of the various factors affecting this cell, with the object of improving its operation. The history of its development is given in detail and the views of various investigators concerning the reactions which take place in the cell are included. G. discusses the mechanism of variation in e. m. f. on discharge and on open circuit. One of the causes which contribute toward high internal resistance is contact resistance between the conductors and the electrodes, and between the porous mass and the C electrode, both of which can be greatly minimized by proper construction and more attention to the method of pressing the porous mass upon the C electrode. A series of expts. is described, in which cells are constructed from materials obtained from various sources and used in varying proportions; and the following conclusions are reached: (1) The envelopment of the electrodes, the C core, and the arrangement of the negative poles is of slight influence on the elec. behavior of the cell. (2) The value of the graphite used depends more on the impurities, % fatty matter and cond. than upon content. A number of samples were examd.: Ceylon natural, 99 and 94% C; Bavarian natural, 82.5 and 92% C; Madagascar natural, 92% C; Korean natural, 90% C; Bohemian natural, 50% C; an artificial graphite, 99% C and Acheson graphite, 99% C. The Korean material gave the best characteristics, with the *manufd. graphite* next. (3)  $\text{MnO}_2$  from various sources was examd.: Caucasian, 84.36 and 89.07% C; Thuringian 72.5%; Brazilian 71.86 and 76%; artificial 69% and a sample of unknown origin, contg. 91.42%  $\text{MnO}_2$ . Here again, the  $\text{MnO}_2$  content is not important, since the artificial material gave the best results. (4) In general, the output, current capacity, and

recovery of a cell increase with increasing fineness of graphite and  $\text{MnO}_2$ . (5) A porous mass contg 5 parts by wt of pyrolusite to 1 part of graphite showed the most favorable results. The mixture should be very intimate and should be applied to the C with the highest pressure practicable. H. STOERTZ.

Hydrogen as a cooling medium for electrical machinery. E. KNOWLTON, C. W. RICE and E. H. FREIBURGHOUSE. *J. Am. Inst. Elec. Eng.* 44, 724-34 (1925). C. G. F.

The electrolytic oxidation of alcohols. II. Chlorination of ethyl alcohol. SHUNO KOIDZUMI. *Mem. Coll. Sci. Kyoto Imp. Univ.* 8A, 155-66 (1925).—Fifty cc. of EtOH was electrolyzed 1 day at 70-80° in a bath of 250 cc. concd. KCl soln. with a C anode and 8 amp per sq dm. The anode was enclosed in a porous cell of special clay and kaolin compn. and a reflux condenser attached. The main products were chloral hydrate, chloral alcoholate and chloroacetic acid. Slow addition of EtOH favors the production of chloral. The intermediate stages are chloroaldehyde alcoholate, its hydrate, and chloroether. Chloroacetal was not found. Tables of results under varied conditions and an outline for the chlorination process are given. J. T. STERN.

The disintegration of carbon anodes in aqueous solutions of nitric acid. H. J. M. CREIGHTON and W. H. OGDEN. *Trans. Am. Electrochem. Soc.* 48, preprint (1925).—Upon the electrolysis of strong aq. solns. of  $\text{HNO}_3$  between C electrodes the anodes disintegrated explosively. Exptl. investigation indicates that the explosions are probably due to a pressure developed in the interior pores of the C anode, as a result of the combined action of the acid and electrolytic oxygen on the carbon. Possibly graphitic acid is formed in the earlier stages of electrolysis and subsequently explodes, forming  $\text{CO}$ ,  $\text{CO}_2$  and water. C. G. F.

A simple mercury arc lght. HELMUT NAUMANN. *Z. tech. Physik* 6, 268-9 (1925). J. H. PERRY.

Electric batteries. BRITISH THOMSON-HOUSTON Co, LTD. *Brit.* 228,147, Jan. 21, 1924. Structural features.

Electric batteries. R. SACHS. *Brit.* 227,396, Sept. 30, 1924. Structural features. Storage battery. O. A. OLSON. U. S. 1,543,787, June 30. An electrolyte is used comprising kieselguhr mixed with  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{Ni NH}_4$  sulfate and NaCl.

Grid plates for storage batteries. H. KELLER. *Brit.* 227,411, Jan. 10, 1924. Mech. features.

Rendering porous electrodes impermeable to liquids. R. OPPENHEIM. U. S. 1,544,030, June 30. Electrodes of C or other porous materials are rendered impervious to liquids by applying Zn "ole-margarate" or other metallic soap to the material of the electrode so that it constitutes a colloidal pectized film, which is not decomposable by the elec. current and is permeable to gases. Electrodes thus treated are adapted for use as depolarizing battery elements.

Apparatus for forming continuous electrodes for electric furnaces. A. HELFENSTEIN. U. S. 1,544,151, June 30.

Electric resistance furnace. L. J. HANCOCK and T. R. HANCOCK. *Brit.* 227,223, Oct. 23, 1923. Cf. C. A. 19, 1382.

Operating electric arc furnaces. W. DYRSSEN. U. S. 1,543,908, June 30. An approx. const. e. m. f. is maintained at the arc regardless of variations in the transformer voltage, and the amperage is varied to control the magnitude of the power input. This method of operation is adapted for use in melting steel or Fe scrap, etc.

Electric resistance furnace for melting brass. O. A. COLBY. U. S. 1,543,695, June 30.

Electric resistance furnace for heat-treatment of round bars, etc. W. J. MERTEN. U. S. 1,543,719, June 30.

Electric furnace electrodes (baked in the furnace in which they are used). NORSKE AKTIESELSKAB FOR ELEKTROKEMISK INDUSTRI NORSK INDUSTRI-HYPOTEK-BANK. *Brit.* 227,820-1-2, Jan. 17, 1924. Structural features.

Electrolytic oxidation and reduction. C. J. THATCHER. U. S. 1,544,357, June 30. "Acceptors" such as anthracene and azoxybenzene, resp., are introduced into the anolyte and catholyte liquors of an electrolytic app. for resp. oxidation and reduction which are assisted by anodic and cathodic catalyzers such as products formed by electrolysis of a soln. of  $\text{Na}_2\text{Cr}_2\text{O}_7$  and  $\text{H}_2\text{SO}_4$ .

Electrolysis of alkali metal chlorides. C. F. VAUGHN and R. E. GEGENHEIMER. U. S. 1,544,078, June 30. After electrolysis of a chloride soln. with a Hg cathode, the soln. is resatd. with salt contg. impurities such as Fe which would be active during the electrolysis, but these impurities are removed during the resatn. of the soln. and before it is further electrolyzed.

**Electrolytic refining of metals.** F. F. COLCORD. U. S. 1,544,726, July 7. Sulfite lignose is added to acid electrolytes for deposition or refining of metals such as Pb, Cu or Sn.

**Electrodeposition of metals.** H. A. SEDGWICK and P. J. SHEEHAN. U. S. 1,544,605, July 7. The elec. resistance of an electrolyte is reduced by conserving in it practically the total quantity of heat generated by the passage of elec. current through it.

**Electrodeposition of chromium.** C. HAMBUECHEN. U. S. 1,544,451, June 30. An electrolyte is used contg. chromic acid in excess (and free from other acids) together with a sol. metal fluoride such as NaF.

**Electrolytic recovery of copper and tin from bronze.** O. SCARPA. Brit. 227,125, Jan. 5, 1924. In the recovery of Sn and Cu from bronze by electrodeposition of the Cu in a  $\text{CuSO}_4$  bath, the spent electrolyte contg. oxygenated Sn compds. in colloidal soln. is withdrawn from the cell and heated, and is either dild. or its acid content is partially or completely neutralized (e. g., by use of NaOH or Cu oxide, hydroxide or carbonate) to ppt. or coagulate the Sn compds.

**Producing copper sheets electrolytically.** W. W. McCORD. U. S. 1,543,861, June 30. Metal is added to a circulating electrolyte, in part of the app., to maintain an approx. const. metallic content in the electrolyte.

**Electrolytic production of iron oxide pigments.** MAGNETIC PIGMENT CO. Brit. 227,319, March 31, 1924. A satd. NaCl soln. is electrolyzed with an Fe anode to produce an Fe salt and alkali. These are separately withdrawn and then recombined outside the electrolytic cell to ppt.  $\text{Fe}(\text{OH})_3$ , which is then subjected to regulated oxidation in the mother liquor to produce pigments.  $\text{Na}_2\text{SO}_4$ , NaBr or NaOAc or KCl also may be used as electrolytes to produce pigments of different shades of color. An app. is described.

**Electrolyzing fused salts.** E. A. ASHCROFT. U. S. 1,545,385, July 7. A melt such as chloride of Pb or Zn is decomposed simultaneously at electrolytic couples in elec. series below the surface of the fused electrolyte.

**Apparatus for electrolyzing fused salts.** E. A. ASHCROFT. U. S. 1,545,383, July 7. The app. is adapted for electrolyzing Zn or Pb chlorides to produce Cl and metal. U. S. 1,545,384 specifies an app. also adapted for electrolyzing fused salts.

**Reducing gases.** A. FOSS, B. F. HALVORSEN and N. STEPHANSEN. U. S. 1,545,419, July 7. Reducing gases are prepd. by the action of an elec. arc on a mixt. of S vapor or pyrites and gaseous O compds. such as  $\text{CO}_2$ .

**Apparatus for electric precipitation of suspended particles from gases.** SIEMENS-SCHUCKERTWERKE GES. Brit. 227,450, Jan. 9, 1924.

**Apparatus (with concrete electrodes) for electric precipitation of suspended particles from gases.** LONGE-COTTRELL, LTD. Brit. 228,073, July 28, 1924.

**Apparatus for electrolytic recovery of values from ores of gold, silver or other precious metals.** W. R. DODGE. U. S. 1,544,227, June 30.

**Electric purification of water or other liquids.** M. D. AVERY. U. S. 1,544,052, June 30. A confined body of the liquid to be purified is rotated by the effect of its velocity, between oppositely polarized surfaces.

**Electric ozone generator.** H. B. HARTMAN. U. S. 1,544,838, July 7.

**Chromium plating.** H. C. PIERCE and C. H. HUMPHRIES. U. S. 1,545,196, July 7. A bath for electrodeposition of Cr comprises chromic acid and relatively small proportions of hydrated chromic hydroxide and  $(\text{NH}_4)_2\text{SO}_4$  in aq. soln.

**Electroplating apparatus.** C. G. MILLER. U. S. 1,545,268, July 7.

**Electrotype plate of copper coated with iron.** H. A. HERR. U. S. 1,544,579, July 7.

**Filaments of electric incandescent lamps.** NAAMLOOZE VENNOOTSCHAP PHILIPS' GLOELAMPENFABRIEKEN. Brit. 228,131, Jan. 24, 1924. Filaments of helical form and consisting of single crystal wire are built up by heating in the vapor of a dissociable compd. of the same metal.

**Electric resistances.** T. A. F. HOLMGREN. Brit. 228,142, Jan. 22, 1924. A resistance material conductive when cold and capable of withstanding very high temps. comprises a mixt. of Si, Ti or similar carbide and a refractory cementing medium such as  $\text{MgO}$ ,  $\text{CaO}$  or other similar oxide. The mixt. is burnt at about  $1200^\circ$  in an atm. of  $\text{CO}$ . Refractory metals or graphite may be added or metals may be pptd. on the pores of the formed material. The product may be in the form of bricks with glazed surfaces.

**Electrolytic condenser, rectifier or lightning arrester cells.** J. SLEPIAN. U. S. 1,543,729, June 30. In cells having electrodes of film-forming material such as Al, Mg or Ti, an electrolyte such as a soln. of  $\text{H}_3\text{BO}_3$  and  $\text{NH}_4$  borate is used together with gelatin, agar agar, albumin, gum arabic or other protective colloid for stabilizing the film.

Electrolytic rectifier. M. A. CODD. Brit 227,303, Oct. 12, 1923. Al and Ta and C may be used for the electrodes.

Rectifiers, etc. NAAMLÖÖZE VENNOOTSCHAP PHILIPS' GLOEILAMPENFABRIEKEN. Brit 227,407, Jan 10, 1924. Incandescing cathodes (yielding an emission of electrons sufficient for the operation of a vacuum tube device at a lower temp. than electrodes of W) are formed of Pt, Ni or similar metal of high m. p. coated with BaO or other alk. earth oxide or of Ni wire superficially alloyed with Ba. The tube may contain A under low pressure.

Electric testing or safety device. B. FIALA-FERNBERG and V. H. WOHL. Brit. 227,832, Jan 18, 1924. A device for indicating high- or low-frequency alternating or intermittent currents or for use as a safety or signaling device comprises a tube of glass, quartz or similar material contg. a "noble gas" under 1-15 (preferably 5) mm. pressure, e. g., Ne with a small addn. of Xe, Kr, A, He or H.

## 5—PHOTOGRAPHY

C. E. K. MEES

The origins of photography in connection with the centennial of its invention. JACQUES BOYER. *La nature* 53, 1, 401-7(1925).—An historical review with portraits of Niepce, Daguerre and Poitevin and with illustrations of the earliest photographs and app.

Sensitometric testing of photo-sensitive materials for positive images by reversal. I. LOBEL. *Bull. soc. franç. phot.* 11, 174-5(1924).—A short method is described for testing the speed of the direct positive compared with that of the plate exposed to give a negative.

An improved method of sedimentary analysis applied to photographic emulsions. F. F. REYNICK AND V. B. SEASE. *2nd Colloid Symposium Monograph* 1925, pp. 37-45.—See C. A. 19, 216.

JEROME ALEXANDER

MIRON, FRANÇOIS. Photographie. 2nd ed. revised by A. Promlo. Paris: Dunod 586 pp. F 54.

Sensitizing photographic films. WESTLAND-FILM Ges. Brit. 227,130, Jan. 5, 1924. A celluloid film coated with a layer of gelatin or rubber is sensitized by a bath contg. dichromate, ferricyanide and KBr.

Motion-picture films. J. E. THORNTON. Brit. 227,199, Oct. 11, 1923. Negative films such as those of the narrow type on ordinary AgBr material are converted into grainless monochrome positive complete pictures by (1) bleaching in a bath which may be formed from K bromide, dichromate, ferricyanide, K alum and glacial HOAc, (2) dissolving out the Ag salts with hypo, (3) washing and drying and (4) dyeing the soft parts of the gelatin to produce the positive images. A plurality of dyes may be used successively to give desired effects of color tone.

Motion-picture films. J. E. THORNTON. Brit. 227,900, Oct. 19, 1923. A monochrome positive film has its images enclosed by cementing together (with their celluloid supports outermost) 2 films of half standard thickness which may carry identical images or images which are complementary or in different shades.

Photographic hardening bath. M. B. PUNNETT. U. S. 1,544,936, July 7. Powd. niter cake and chrome alum are mixed, permitted to dry, and pulverized, to produce a powder for making hardening baths.

## 6—INORGANIC CHEMISTRY

A. K. MIDDLETON

Studies of the double acetates of copper and the alkalies. ERICH BÖTTGENBACH. *Z. anorg. allgem. Chem.* 145, 141-59(1925).—Two double salts with KOAc were prepd.  $\text{Cu}(\text{OAc})_2 \cdot \text{K}(\text{OAc}) \cdot 2\text{H}_2\text{O}$  (green) and  $\text{Cu}(\text{OAc})_2 \cdot 3\text{KOAc}$  (ultramarine blue). They decompose readily in  $\text{H}_2\text{O}$  or on heating. They are practically insol. in org. solvents.

Non-existence of the double sulfate,  $\text{MnK}_2(\text{SO}_4)_2$ . G. CARONNI AND V. CAGLIOTTI. *Gazz. chim. ital.* 55, 411-3(1925).—See C. A. 19, 943.

The monoclinic sulfates containing thallium. Thallium nickel and thallium cobalt sulfates. A. H. H. TURTON. *Proc. Roy. Soc. (London)* 108A, 240-61(1925);

of C. A. 4, 2775.—Of Ti salts of the series  $R_2M(S_2Se)_2O_4 \cdot 6H_2O$  only the Ti Zn sulfate and selenate had been obtained in crystals sufficiently perfect for the purposes of T's investigation. Owing to the slight soly of  $Ti_2SO_4$ , very dil. solns. of the mixed sulfates must be employed and  $Ti_2SO_4$  tends to sep. instead of the double salts. Even when these are obtained, distortion and twinning usually make the crystals useless. The net result of thousands of preps., including Fe, was two crops of remarkably perfect crystals of the Ni salt and two crops of the Co salt. T can offer no reason for success in these cases as practically ideal conditions were maintained in all attempts. The net result of the very complete optical exams. reported is to confirm the conclusions drawn from examn. of the Ti Zn salts, that Ti, like  $NH_4$ , does not belong to the inner eutropic series of the alkali metals, and that it is distinguished by its outstandingly high refractive and dispersive power. A. R. M.

Compounds of trivalent molybdenum. III. New oxalates. W. WARDLAW AND W. H. PARKER. *J. Chem. Soc.* 127, 1311-8 (1925) cf. C. A. 19, 618.—To 50 g. of  $H_2C_2O_4 \cdot 2H_2O$  in 300 cc. water was added the  $Mo(OH)_3$  from 40 g. of  $MoO_3$ , reduced as in C. A. 19, 20, and the mixt. boiled down to 100 cc. in a rapid current of  $N_2$ . The golden brown liquid was cooled to room temp. and the excess of acid which crystd. out, removed. The soln. was electrolyzed 12 hrs. at 4 v. and 0.05 amp. per cm.<sup>2</sup> and the resulting liquid forced by  $N_2$  pressure into 1 l. of pure dry acetone whereupon a finely divided brown powder sep'd. Analysis indicated a new oxoxalate  $MoO(C_2O_4) \cdot 6H_2O$  remarkably similar in properties and mode of decompn. to the oxysulfate previously described. Decompn. of this compd., or prolonged boiling of a soln. of  $Mo(OH)_3$  in oxalic acid, yields the insol. oxoxalate  $MoO_2(C_2O_4) \cdot 12H_2O$  bright red brown showing the same reducing properties. Air oxidation of these compds. in presence of water yields a red soln. from which EtOH ppts. molybdenyl oxalate  $MoO(C_2O_4) \cdot 3H_2O$  red powder very hygroscopic, very sol. in water to a magenta soln. quite stable in air. For this the formulation  $[Mo_2O_7(C_2O_4)]H_2$  is suggested. The  $C_2O_4$  radical is in a complex ion in all these compds. of quadrivalent Mo. A. R. M.

Molybdenum pentoxide. W. WARDLAW AND F. H. NICHOLLS. *J. Chem. Soc.* 127, 1487-8 (1925).—Pure  $MoO_5$  is readily prep'd by carefully heating the oxysulfate or oxoxalate (preceding abstract) in a current of  $N_2$ . It is violet-black. It remained almost unchanged after being boiled with 5 successive portions of  $NH_4OH$ , washed with water and dried at  $110^\circ$ , contrary to Guichard (*Compt. rend.* 129, 722 (1899)). The analytical compn. remained unchanged but Mo could be detected in the  $NH_3$  ext. The pentoxide is difficultly sol. in  $HCl$  and  $H_2SO_4$ . A. R. M.

Osmium tetroxide. II. Compounds of osmium tetroxide. F. KRAVSS AND D. WILKEY. *Z. anorg. allgem. Chem.* 145, 151-67 (1925) cf. C. A. 18, 3564.—Abegg's theory assumes that an element cannot combine with more than 4 atoms of O, as illustrated in the ortho acids,  $H_2SiO_4$ ,  $H_2PO_4$ ,  $H_2SO_4$ ,  $HClO_4$ , and therefore that octavalent Os and Ru in  $OsO_4$  and  $RuO_4$  are coordinately sat'd. However K. and W. prep'd the following double compds. in well-formed reddish brown or yellow crystals:  $OsO_4 \cdot 2CsOH$ ;  $OsO_4 \cdot 2KOH$ ;  $OsO_4 \cdot 2NH_4OH$ ;  $OsO_4 \cdot Ba(OH)_2$ ;  $OsO_4 \cdot 2CaF_2$ ;  $OsO_4 \cdot 2RbF$ , by pouring a soln. of the base or salt over solid  $OsO_4$ . These compds. soon dissociated into their constituents.  $OsO_4$  exists in 2 modifications, (a) white needles, sol., reactive, m.  $39.5^\circ$ , giving on cooling (b) yellow needles, difficultly sol., unreactive, m.  $41^\circ$ ; b.  $134^\circ$ , giving (a) on sublimation, or by cooling with liquid air. A. W. FRANCIS.

Complex tin iodides. V. AUGER AND T. KARANTASSIS. *Compt. rend.* 180, 1845-7 (1925).—Iodostannates of the type  $MSnI_4$  are obtained only when M = Rb or Cs or an org. base as  $N(CH_3)_3$ , or with similar iodides as  $(CH_3)_4NI$  or  $(CH_3)_4AsI$ . Stable addn. compds. with similar bromides have also been found, but none so far with chlorides. Prepn. and analysis are given. J. T. STERN.

New complex iron compounds derived from triazines. PAUL PASCAL. *Compt. rend.* 180, 1850-1 (1925).— $Fe(C_2N_3)(CO_3)_2 \cdot K_2 \cdot 24H_2O$  is a yellow-orange poorly sol. salt which liberates little ferric ion in aq. soln. With more ferric salt,  $Fe(CNCO_2)_2 \cdot Fe + 4Fe(CNCO_2)_2 \cdot K_2 \cdot 40H_2O$  crystallizes out. A color change to brown occurs in the light, slowly reversible in the dark. The corresponding ferrous salt is reddish and with excess of Fe gives an indigo-blue ppt. of  $[Fe(CNCO_2)_2]K_2Fe \cdot 24H_2O$ . Its soln. is cochineal-red and contains free ferrous ions. Decompn. into oxalate,  $NH_3$  and Fe occurs very easily. J. T. STERN.

A new type of alkali borate; the pentaborates. V. AUGER. *Compt. rend.* 180, 1862-4 (1925).—K. pentaborate, corresponding to the empirical formula  $K_2B_5O_{11} \cdot 5H_2O$  is formed by crystn. from a soln. of K. tetraborate contg. an excess  $B_2O_3$  approx. in the ratio 2.5  $B_2O_3$  to 1 K, provided the crystn. is carried out between  $115^\circ$  and  $120^\circ$ . The

salt is also formed by heating a concd. soln. of K tetraborate in a sealed tube for 10 hrs at 115–120° and subsequently seeding the soln. with a crystal of the pentaborate. On heating the salt to 360°, 4 mols of  $H_2O$  are lost. It is necessary to heat above 400° to remove the fifth  $H_2O$  mol. It is probable that the salt is really an acid salt of the acid  $H_2B_5O_{11}$ , and should be represented by the formula  $K_2HB_5O_{11} \cdot 2H_2O$ . It is only slowly attacked by hot water. The Na salt,  $Na_2HB_5O_{11} \cdot 2H_2O$ , is formed in the same way, but cannot be obtained pure as it is rapidly transformed by  $H_2O$  to borax. Li pentaborate could not be formed. R. L. DODGE

An artificial magnesium silicate. A. DAMIENS, *Compt. rend.* 180, 1843–5 (1925).—When a soln. of Na silicate is pptd. with  $MgSO_4$ , no definite compd. is obtained, and part of the Mg Na silicate stays in colloidal soln. In fractionating the deposit, it yields silicates from  $2SiO_2(MgNa_2)O$  to  $SiO_2(MgNa_2)O$ . J. T. STERN

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VÉCHOT, JACQUES: Étude sur les sels de plascéénazonium. Paris: Les Presses universitaires de France. 78 pp.

## 7—ANALYTICAL CHEMISTRY

WILLIAM T. HALL

The analytical chemical use of Röntgen spectroscopy. P. GÜNTHER, *Z. anorg. Chem.* 37, 355–7 (1924).—The method depends upon counting the Ag grains on the photographic plate in the spectrum lines. Analyses accurate to within 2% are claimed (For Zr and Hf, cf. Coster and Nabina, *C. A.* 19, 2000.) G. L. CLARK

Preparation of Nessler's solution. H. D. RICHMOND, *Analyst* 50, 67 (1925).—Dissolve 17.5 g. KI in 100 cc. of water and mix with a soln. of 15 g.  $HgCl_2$  in 300 cc. of water. Wash the resulting ppt. and dissolve it in a soln. of 17.5 g. KI in 100 cc. of water, adding finally enough  $HgCl_2$  to produce a very slight ppt. Dil. to 500 cc., cool in ice water and add 400 cc. of water contg. 105 g. of NaOH. Cool, make up to 1 l. and decant the clear soln. after standing. W. T. H

Simplified method of micro-combustion: the micro-Dannstedt method. C. FUNK AND S. KON, *Science* 61, 659 (1925).—In the micro-Dumas method according to Pregl too high results were obtained but good results were obtained by the method of Dubsky. For the detn. of C and H, only 10% of the results were correct by the Pregl method but nearly 100% were correct by the Dannstedt method. W. T. H

Action of some oxidizing agents on sulfite. H. W. S. HENDRIXSON, *J. Am. Chem. Soc.* 48, 2156–9 (1925); cf. *C. A.* 19, 1830.—If sulfite is titrated directly with bromate, dichromate or permanganate, the results are always low but if iodate alone or KI together with one of the above oxidizers is used, the results are accurate. The theory advanced is that the free  $I_2$  formed by the action of oxidizer on KI in acid soln. is really the effective agent in the oxidation of  $SO_3^{--}$ .  $Br_2$  can be used as titrating agent but  $KBrO_3$  and  $KBr$  are not efficient because the  $Br_2$  is liberated too slowly. W. T. H

Differential electro-titration. D. C. COX, *J. Am. Chem. Soc.* 47, 2138–43 (1925).—If a soln. to be titrated is divided exactly into halves, the halves are placed in 2 similar beakers each of which contains a coiled Pt wire to serve as electrode, and elec. contact between the solns. is maintained between the solns. by means of wires which pass through a potentiometer or nullvoltmeter and also by means of a salt bridge, then by titrating each soln. simultaneously in such a way that one is kept 0.2 cc. in advance of the other, the end point is obtained when the max. e. m. f. exists between the 2 solns. In this way an electrometric titration is accomplished very easily without the aid of a standard cell. The method is illustrated by several alkalimetric and acidimetric titrations. W. T. HALL

Determination of suspensoids by alternating-current precipitators. P. DRINKER AND R. M. THOMSON, *J. Ind. Hyg.* 7, 261–71 (1925).—The construction and adaptation of portable a.-c. precipitators to the detn. of such suspensoids as dusts, fumes and smokes are discussed and the difference between the a.-c. method using glass collecting electrodes and the Cottrell process with rectified current and metal collecting electrodes is pointed out. Poor results obtained with small precipitators are often due to failure to distinguish between conducting and non-conducting suspensoids. A portable storage-battery, induction-coil type of precipitator is described and illustrated. The method

of inserting a celluloid foil in the collecting electrode and catching therewith some of the ppt for microscopical study is described. Such foils or the entire electrode can be mailed or otherwise transported and representative slides made up later in the lab.

W. T. H.

Sodium arsenite, the reagent for loosely bound, reactive oxygen sulfur and nitrogen. A. GUTMANN. *Z. anal. Chem.* 66, 224-42(1925).— $\text{Na}_2\text{AsO}_3$  reacts with quadrivalent, loosely bound O (peroxides), S (persulfides and polysulfides) and with quinquevalent and trivalent N in org azido compds. Compds contg O of this type, which were found to react with  $\text{Na}_2\text{AsO}_3$  are  $(\text{NaSO}_3)_2$ ,  $\text{O SC}_2\text{H}_5$ ,  $(\text{CH}_3\text{C}_2\text{H}_4)\text{SO}$ ,  $\text{O SC}_2\text{H}_5$ ,  $\text{C}_2\text{H}_5(\text{CH}_2)_2\text{N}\cdot\text{O}\cdot$ , quinine oxide, oil of turpentine,  $\text{NO}$ ,  $\text{C}_4\text{H}_9\text{NO}$ ,  $\text{CH}_3\text{N}(\text{NO})\text{CO}_2\text{C}_2\text{H}_5$ ,  $\text{C}_2\text{H}_5(\text{SO}_2\text{OH})\text{N}\cdot\text{ONa}$ ,  $\text{C}_4\text{H}_9\text{N}(\text{COCH}_3)\text{NO}$ ,  $\text{C}_4\text{H}_9\text{N}(\text{CO C}_2\text{H}_5)\text{NO}$ ,  $\text{NO O O C}_2\text{H}_5$ ,  $\text{C}_2\text{H}_5(\text{ONO})_2$ ,  $\text{C}_2\text{H}_5\text{NO}_2$ ,  $\text{C}_2\text{H}_5\text{O Cl}$ ,  $\text{NH}_2\text{OH}$ ,  $\text{C}_2\text{H}_5\text{NHOH}$ ,  $\text{C}_2\text{H}_5\text{NHOH}$  and  $\text{N}:\text{CH N C O}$ .

$\text{C}_2\text{H}_5$ . Compds contg S which were found to react with  $\text{Na}_2\text{AsO}_3$  are  $\text{C}_2\text{H}_5\text{S}$ ,  $\text{SC}_2\text{H}_5$ ,  $\text{NCS}$ ,  $\text{SCN}$ ,  $\text{C}_2\text{H}_5\text{S SCN}$ ,  $\text{S}(\text{CN})$ ,  $\text{C N}$ ,  $\text{Cu}(\text{SCN})_2$ ,  $\text{S}(\text{C}_2\text{H}_5)$ ,  $\text{C N}$  and  $\text{C}_2\text{H}_5\text{NCS}$ . Of

S compds. corresponding to the polysulfide class, the following react with  $\text{Na}_2\text{AsO}_3$ :  $\text{Na}_2\text{S}_2\text{O}_3$ ,  $\text{C}_2\text{H}_5(\text{CH}_2)_2\text{S}_2\text{O}_3\text{Na}$ ,  $\text{CuS S Cu}$ ,  $(\text{CSOC}_2\text{H}_5)_2\text{S}$ ,  $\text{S}(\text{CSOC}_2\text{H}_5)$  and  $(\text{CH}_3\text{CO})_2\text{S}$ .  $\text{S}(\text{COCH}_3)$ . Compds. contg. loosely bound, quadrivalent O and similarly bound S, which react with  $\text{Na}_2\text{AsO}_3$  are  $(\text{SO}_2\text{Na})_2\text{S O O S}(\text{SO}_2\text{Na})$ ,  $(\text{SO}_2\text{Na})_2\text{S O O}(\text{SO}_2\text{Na})$ . Compds. contg. loosely bound S in the polysulfide and in the persulfide states, which react with  $\text{Na}_2\text{AsO}_3$  are  $\text{CH}_3(\text{S}_2)\text{CH}_3$ , and  $\text{NC S S CN}$ . Compds. of the azide type



which were tested are  $\text{C}_7\text{H}_7\text{N}_3$ ,  $\text{C}_4\text{H}_9\text{CON}_3$  and  $\text{C}_2\text{H}_5\text{N}_3$ .

W. T. H.

Qualitative test for weak bases. R. ROBINSON. *J. Chem. Soc.* 127, 768-9(1925).—The "weak bases" are C compds. contg. O, N or S. The test is shown by most simple alcohols, aliphatic ethers, ketones, aldehydes, phenol ethers, nitro compds., nitriles, thioethers, etc. It consists in dissolving the org substance in petroleum ether and adding a satd. soln. of  $\text{FeCl}_3$  in concd.  $\text{HCl}$ . Three layers often result; the lowest is the aq. soln. of  $\text{FeCl}_3$  and  $\text{HCl}$ , the green or brown middle layer is a ferrichloride of the "weak base" and the upper layer is chiefly petroleum ether. By means of this behavior it should be possible to remove traces of oxygenated and nitrogenous compds. from hydrocarbons. Camphor oil contains safrole and camphor; if the mixt is dissolved in petroleum ether and  $\text{HCl}\cdot\text{FeCl}_3$  added, a green middle layer is obtained from which solid camphor can be obtained by adding water.

W. T. H.

Exact gas analysis methods. The determination of the higher hydrocarbons. E. OTT. *Gas u. Wasserfach* 68, 367-9(1925).—Fuming  $\text{H}_2\text{SO}_4$  is preferable to  $\text{Br}\cdot\text{H}_2\text{O}$  as an absorbent for  $\text{C}_2\text{H}_2$  or  $\text{C}_2\text{H}_4$ , being more convenient and giving lower errors due to incomplete absorption, O from the medium itself, etc.; six 3-min. passes with a pipet filled with glass rods are recommended. Ammoniacal  $\text{CuCl}$  gives the best results for CO if used in small quantities, i. e., 2 cc. of fresh soln. per pass; the error in the analysis of 98.9% CO by this method was only 0.04%.

WM. B. PLUMMER

New analytical method for the examination of gas from roasting ovens. H. GRÜSS. *Z. angew. Chem.* 38, 488-9(1925).—The heat cond. of  $\text{SO}_2$  is only about 0.34 that of  $\text{N}_2$  or of  $\text{O}_2$ . If  $\text{SO}_2$  is present in a mixt. of  $\text{N}_2$  and  $\text{O}_2$ , the quantity can be detd. by measuring the cond. of the gas. In this way values of 9.05, 7.05 and 5.45%  $\text{SO}_2$  were obtained when titration by the method of Reich gave 9.02, 7.08 and 5.49%  $\text{SO}_2$ . A simple app. is described, made by Siemens and Halske of Berlin, in which the heat cond. is measured by detg. the elec. resistance of a wire heated electrically in a current of gas.

W. T. H.

Gas analysis. LEBEAU. *Chaleur et industrie* 6, 236-45(1925).—An address on methods of gas analysis used in research labs., with examples of their application.

A. PAPINEAU-COUTURE

Report on nitrogen. A. L. PRINCE. *J. Assoc. Official Agr. Chemists* 8, 410-7(1925).—Collaborative expts. at 21 different stations show that most operatives get just as good results with the Devarda-alloy method as with the more complicated Moore-Kjeldahl method. It is recommended that the Devarda alloy be adopted as tentative method. The substitution of  $\text{Na}_2\text{S}_2\text{O}_3$  for  $\text{K}_2\text{S}$  or  $\text{Na}_2\text{S}$  to ppt. Hg in the Kjeldahl method appears to be permissible.

W. T. H.

Report on potash. A. P. KERR. *J. Assoc. Official Agr. Chemists* 8, 419-20(1925).—The detn. of  $\text{K}_2\text{O}$  in fertilizers by the "water-insol." method sometimes gives

low results. The trouble is often due to the presence of  $\text{PO}_4^{---}$  in the soln. after the addn. of  $\text{NH}_4\text{OH}$  and  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  and can be overcome by adding 25 cc. of 1%  $\text{MgCl}_2$  soln. before adding the  $\text{NH}_4\text{OH}$ . W. T. H.

Modification of the official Lindo-Gladding method for the determination of potash. C. M. BIBLE. *J. Assoc. Off. Agr. Chemists* 8, 420-3 (1925).—To overcome the error produced by  $\text{PO}_4^{---}$ , it is recommended to add  $\text{MgO}$  after the pptn. with  $\text{NH}_4\text{OH}$  and  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ . W. T. H.

Comparative study of the Gunning-Arnold and Winkler boric acid modifications of the Kjeldahl method for the determination of nitrogen. K. S. MARKLEY AND R. M. HANN. *J. Assoc. Off. Agr. Chemists* 8, 455-67 (1925).—Extensive tests show that it is equally accurate and in many respects advantageous to use a 5% soln. of  $\text{H}_3\text{BO}_3$  for absorbing  $\text{NH}_3$ , as recommended by Winkler, instead of a standard soln. of acid. A comparison of the  $\text{CuSO}_4 \cdot \text{P}_2\text{O}_5$  digestion method with that of  $\text{HgO} \cdot \text{K}_2\text{SO}_4$  shows that the former is satisfactory although with alkaloïds it requires more time. W. T. H.

Determination of oxides of nitrogen (except nitrous oxide) in small concentration in the products of combustion of coal gas and in air. A. G. FRANCIS AND A. T. PARSONS. *Analyst* 50, 262-72 (1925).—The method of Allison, Parker and Jones (*C. A.* 16, 34), for detg. oxides of N in which  $\text{NaOH}$  and  $\text{H}_2\text{O}_2$  were used as absorbents, proved to give results that were below the truth. The chief difficulty was due to incomplete oxidation by means of  $\text{H}_2\text{O}_2$  in alk. soln. The method as modified is: Aspirate the gas to be analyzed through a bottle of known capacity. After collecting the sample in the bottle, add 7 cc. of acidulated  $\text{H}_2\text{O}_2$  (50 cc. of 7.5%  $\text{H}_2\text{O}_2$  and 1 cc. of 2 N  $\text{H}_2\text{SO}_4$  mixed and dild. to 100 cc.) Stopper the bottle and let it stand for 3 hrs. with frequent rotation. Rinse the soln. into a flat porcelain dish, make barely alk. with  $\text{KOH}$  and evap. to dryness. Cool, moisten the residue with 2 cc. of phenoldisulfonic acid reagent, dil., make ammoniacal with 15 cc. of 7.5 N  $\text{NH}_4\text{OH}$  and compare the color with standards similarly treated. This method is applicable for detg. NO present in proportion over 1 part per million. The analysis of 13 samples of gas all showed higher values than with the defective method of Allison, Parker and Jones, the av. error being more than 100%. The method can be applied to even smaller quantities of NO if the dried gas is passed through a tube chilled by liquid air. The NO condenses with the  $\text{CO}_2$  and the condensate can be analyzed as above described. W. T. H.

Rapid qualitative and quantitative analysis of commercial hydrogen peroxide. A. QUARTAROLI. *Ann. chim. applicata* 15, 32-5 (1925).—The test is based on recently published work of Q. on the decompn. of  $\text{H}_2\text{O}_2$  by  $\text{CuO}$  (*C. A.* 19, 1525), the reagent being 0.15%  $\text{CuSO}_4$  soln. and 20%  $\text{NaOH}$  soln. To 20 cc. of  $\text{H}_2\text{O}_2$  add 2 cc. of  $\text{CuSO}_4$  and 2 cc. of  $\text{NaOH}$ . If the evolution of O is slow and continuous and a slight brownish ppt. is formed, the  $\text{H}_2\text{O}_2$  contains 6-12 vols. of O, but if the evolution is tumultuous with a grayish green ppt., the concn. is 3 vols. or less of O. If the  $\text{H}_2\text{O}_2$  is extremely weak, evolution of O is rapid but only momentary and a blue ppt. is formed. With 1.5%  $\text{CuSO}_4$  the ppts. are greater in amt. and under these conditions the ppt. with  $\text{H}_2\text{O}_2$  contg. 10-12 vols. of O is black at first, changes after several hrs. to green and then to blue. With  $\text{H}_2\text{O}_2$  contg. 6 vols. of O the change from black occurs in an hr., with  $\text{H}_2\text{O}_2$  contg. 3 vols. the ppt. changes to green and blue in 10-20 min. and it still more dil. a point is reached where the ppt. is blue at first. With the aid of these phenomena the original strength of a sample of  $\text{H}_2\text{O}_2$  can be estd. by first dilg. it. To make the test quant., dil. the  $\text{H}_2\text{O}_2$  with  $\text{H}_2\text{O}$  to 4 times its vol., add to 20 cc. of this 2 cc. of 1.5%  $\text{CuSO}_4$  and 2 cc. of 20%  $\text{NaOH}$  and measure the vol. of O evolved. This test can be done accurately enough for com. work with a test tube connected with a graduated U-tube or ureometer. Evolution is rapid and complete without heating and the test is simpler and more reliable than titration with  $\text{KMnO}_4$ . C. C. DAVIS

Congo red as a reagent for boric acid. J. STAMM. *Pharmazie* 1924.—The color of Congo red paper is unchanged on moistening with 4% boric acid soln., but a blue coloration is produced by cautiously heating over a small flame, or, to a less marked extent, by drying in a desiccator or at  $100^\circ$ . The red color is restored on exposing the dried paper to moist air. With boric esters, the blue coloration is only produced if the paper be previously moistened. A more delicate test consists in adding a drop of boric acid soln. to a drop of 0.1% Congo red soln., and evapg. to dryness on a water bath. The blue residue dissolves in water, alc.,  $\text{MeOH}$ , or acetone, yielding a red soln. The color change is detectable with 0.1 cc. of 0.01% boric acid soln. The reaction is characteristic of boric acid among acids, but certain Zn, Al, Mn, Mg,  $\text{NH}_4$ , Ni, Co and ferrous salts produce the same effect, and these metals must be eliminated before applying the test, or the boric acid must be converted into an ester. The blue coloration is due

to the formation of metaboric acid, and on heating to 140–160° to convert the acid into pyroboric acid, the red coloration returns B. C. A.

**Determination of phosphoric acid as magnesium ammonium phosphate.** GUNNER JØRGENSEN. *Z. anal. Chem.* 66, 209–24 (1925).—McCandless and Burton (*C. A.* 3, 451) have published a method based on the pptn. of  $MgNH_4PO_4$  in the cold. To show the inaccuracy of such a method, expts. carried out in 1904 by J. are cited. D. Balarev (*Z. anal. Chem.* 64, 276 (1924)) has claimed that J.'s method is inaccurate, and to this statement also exception is taken W. T. H.

**The analysis of fluorspar.** P. DRAWE. *Chem.-Ztg.* 49, 497 (1925).—Use 4 samples each weighing about 1 g. The first serves for the detn. of  $SiO_2$ ,  $Fe_2O_3$ ,  $Al_2O_3$ ,  $MnO$  and total  $CaO$ , the second for the detn. of  $CaO$  not present as fluoride and for  $SO_2$  present as  $CaSO_4$ , the third for the detn. of  $CaCO_3$ , and the fourth for the loss on ignition. (1) Digest the sample in a Pt dish with  $HF$  until all  $Si$  is volatilized as  $SiF_4$ . Then moisten with  $NH_4OH$ , dry, ignite and weigh. The loss in wt. represents  $SiO_2$ , moisture and org. matter. Crush the sintered residue to a powder in a small agate mortar and treat it, in the original Pt dish, with  $H_2SO_4$  until all  $CaF_2$  is decomposed. Heat till most of the excess acid is expelled, transfer to a porcelain dish and boil 15 min. with an excess of soda soln. Filter and dissolve the washed ppt. in dil.  $HCl$ . In the  $HCl$  soln. det.  $Fe$ ,  $Al$ ,  $Mn$  and  $Ca$  in the usual way. (2) Boil the second sample with 10% soda soln. to convert  $Ca$  sulfate and silicate into  $CaCO_3$ , the treatment has very little effect upon  $CaF_2$ . Filter and in the filtrate det.  $SO_2$  to det. the  $CaSO_4$  content. Treat the residue from the soda treatment with dil.  $HCl$  and in an aliquot part ppt.  $Al$ ,  $Fe$  (after oxidation),  $Mn$  and a little dissolved  $CaF_2$  by means of  $NH_4OH$  and det.  $Ca$  in the filtrate. (3) Boil this sample with standard  $HCl$  soln. and titrate the excess acid. (4) Ignite and det. the loss in wt. W. T. H.

**Hahn's iron titration method and Rosenmund's modification.** E. RUPP. *Apoth. Ztg.* 39, 422–3 (1924).—The success of Hahn's and Windisch's iron titration method (*C. A.* 17, 1767) depends on the purity of the thiosulfate solution; an increase in the amt. of  $KI$  is frequently but not invariably of value. At present the usefulness of the method is limited. B. C. A.

**Determination of small amounts of iron by colorimetric methods.** W. B. WALKER. *Analyst* 50, 278 (1925).—The thiocyanate and ferrocyanide methods for the colorimetric detn. of small quantities of  $Fe$  were studied and modified slightly. For the oxidation of  $Fe$ ,  $HNO_3$  contg.  $HNO_2$  is desirable but all  $HNO_2$  should be removed before applying the colorimetric tests. In the thiocyanate method this is best accomplished by adding a little  $H_2O_2$  but in the ferrocyanide method, boiling for a short time is recommended. The thiocyanate process is generally preferable but is unsatisfactory in the presence of  $Ag$ ,  $Hg$ ,  $Co$ ,  $H_3PO_4$ ,  $H_2C_2O_4$ , and  $HF$ . Oxalates and fluorides must be removed in both methods but  $H_3PO_4$  does no harm in the ferrocyanide method. The results of about 40 analyses, mostly of food products, are given with  $Fe$  varying from 0 to 11 parts per 100,000. Good agreement was obtained when both methods were used. W. T. H.

**A simple method for determining potassium.** R. MEURICE. *Ann. chim. anal. chim. appl.* 7, 161–3 (1925).—To a quantity of  $K$  salt corresponding to 0.65 g. in 20–25 cc. of water, add 100 cc. of satd.  $NaHC_2H_3O_2$  and an equal vol. of methanol (used because less expensive than alc. in France). Allow to stand overnight. Wash the ppt. with 50% methanol, dissolve it in a little water and titrate with  $NaOH$  using phenolphthalein as indicator. The presence of  $SO_4$ ,  $NO_3$ ,  $Ca$ ,  $Mg$ , etc., does no harm because the resulting ppts. do not take part in the titration. This simple method is claimed to give better results in the hands of beginners than the well-known  $KClO_4$  method. W. T. H.

**Critical study of the separation of molybdenum from vanadium as sulfide.** A. E. STOPPEL, C. F. SIDENER AND P. H. M. P. BRINTON. *Chem. News* 130, 353–5 (1925).—The sepn. of  $Mo$  from  $V$  as sulfide is accomplished better by pptn. with  $H_2S$  in acid soln. in a pressure flask than by acidifying an ammoniacal soln. which has been satd. with  $H_2S$ . In the former case, there are to be sure traces of  $V$  in the  $MoS_3$  ppt. but this error is compensated by  $Mo$  that fails to ppt. In the other method, the pptn. of  $Mo$  is more complete but the  $MoS_3$  ppt. contains 0.5 mg. or more of  $V$ . There is less pptn. of  $V$  when  $H_2S$  is passed into an ammoniacal molybdate and vanadate soln. than when  $(NH_4)_2S$  is added directly. W. T. H.

**The determination of copper in commercial copper sulfate.** R. BIAZZO. *Ann. chim. applicata* 15, 92–4 (1925).—Dissolve 5.494 g. of com. sulfate in  $H_2O$  in a 250-cc. measuring flask, oxidize any ferrous salts with  $Cl-H_2O$ , boil to eliminate excess  $Cl$ , ppt. the  $Fe$  with excess  $NH_4OH$ , cool, make up to 250 cc. and filter. Add to 50 cc. of the filtrate in a 220-cc. measuring flask enough  $KCN$  soln. to decolorize the liquid and

then add 44 cc. of 0.1 N KSCN. Acidify with dil  $H_2SO_4$ , cool, make up to 220 cc., add 0.3 cc. more of  $H_2O$  to compensate for the vol. occupied by the  $CuSCN$ , filter and titrate 200 cc. of the filtrate with  $KMnO_4$ . Add as much more  $KMnO_4$  as was required in the titration and titrate this with 0.1 N KSCN. If  $x$  is the no. of cc. of the latter necessary for the second titration, the %  $CuSO_4 \cdot 5H_2O$  in the com. sulfate is  $100 - 2.5x$ . If the com. sulfate is fairly pure, 0.02 N or even 0.01 N KSCN may be used to advantage. The method overcomes the disadvantages of the Volhard method and is more accurate. The only source of error arises from the recognized fact that the quantity of  $KMnO_4$  for titrating the excess KSCN is slightly less than the theoretical, a discrepancy which increases with increase in the diln. of the KSCN. This error is avoided by standardizing the  $KMnO_4$  against KSCN of similar concn. to that in the test. C. C. DAVIS

**Colorimetric determination of molybdenum.** E. WENDHORST. *Z. anorg. allg. Chem.* 144, 319-20 (1925).—Collordal  $MoS_3$  has a brownish red to light yellow color which can be used as the basis for the colorimetric detn. of Mo. By means of the method a sample of com.  $MoO_3$  assayed the same as by the usual gravimetric method. For the colorimetric standard,  $MoO_3$  can be prepd. by careful roasting of the freshly pptd. sulfide. Dissolve 0.05-0.1 g. of the oxide in water and a little  $NH_4OH$ . Boil off the excess of the latter and dil to 500 cc. in a measuring flask. Take 15-20 cc. dil with an equal vol. of water and the same amt. or a little more of  $H_2S$  water contg. 5% of glycerol. Finally mix with an equal vol. of 0.2 N  $H_2SO_4$ , adding the acid until the red color no longer deepens. In the analysis, treat the ppt. of  $MoS_3$  obtained in the usual way, with Br water to oxidize all the S and remove the excess Br by boiling. Then treat it in the same way as the standard. Solns. contg. only 0.01 g. Mo per l. can be analyzed in this way. W. T. H.

**Separation of zinc and nickel by means of hydrogen sulfide.** A. KLING, A. LASSEUR AND MIRE A. LASSEUR. *Compt. rend.* 180, 517-9; *Ann. chim. anal. chim. appl.* 7, 163-5 (1925).—To sep. Zn from Ni by means of  $H_2S$  in solns. free from added salts it is necessary to keep the  $pH$  value between 1.35 and 2 and continue passing  $H_2S$  for a long time. This condition is difficult to maintain. W. T. H.

**Carbon error in the quantitative deposition of nickel and iron from complex oxalate electrolytes.** P. K. PROCTOR. *Analyst* 50, 224-30 (1925).—In a series of expts. the deposits obtained electrolytically from oxalate solns. were always too high in the case of Ni but with Fe the presence of  $NH_4Cl$  prevented contamination. For 0.25 g. of Fe as sulfate, 8 g. of  $(NH_4)_2C_2O_4$  and 5 g. of  $NH_4Cl$  in 150-200 cc. of water were used successfully with 1 amp. of current over a period of 12 hrs. with stationary Pt gauze electrodes. W. T. H.

**The use of liquid amalgams in volumetric analysis. II. Oxidimetric determination of tungsten, etc., with the aid of lead and bismuth amalgams.** K. SOMAYA. *Z. anorg. allg. Chem.* 145, 168-80 (1925), cf. *C. A.* 19, 224.—By heating Zn, Pb or Bi with Hg and cooling, a mixt. of solid and liquid amalgams is easily obtained and by means of a separatory funnel, the liquid amalgam can be sepd. from the solid. These liquid amalgams are preferred by S. to amalgamated Zn as commonly used in a Jones' reductor. By means of liquid Pb-Hg in acid soln.,  $Fe^{+++}$  can be reduced to  $Fe^{++}$  and the reduced soln. can be titrated with  $KMnO_4$ .  $TiO_2^{--}$  can be reduced to  $Ti^{+++}$  and the latter titrated with  $KMnO_4$  or with ferric alum.  $UO_2^{++}$  can be reduced to  $U^{+++}$ ,  $MoO_4^{--}$  to  $Mo^{+++}$  and  $WO_4^{--}$  to  $W^{+++}$ . All these reduced solns. can be titrated with  $KMnO_4$ . With liquid Bi-Hg,  $WO_4^{--}$  is reduced quantitatively to the quadrivalent condition. W. T. H.

**Oxidimetric titration of uranium.** O. KONTIC. *Chem. Listy* 19, 1-3 (1925).—When salts of hexavalent U are reduced with the usual metallic reducing agents the greater part of the U is converted into the quadrivalent form, but there is always a certain amt. of a deriv. of a lower oxide produced. Pb, in the presence of  $HCl$ , quantitatively reduces uranyl chloride to  $UCl_4$ , which, after addn. of Mn sulfate and  $H_2SO_4$ , may be titrated with  $KMnO_4$  with good results. B. C. A.

**Determination of small amounts of zinc in materials of organic nature.** A chemical method based on the fluorescence of zinc salts with urobilin. R. E. LUTZ. *J. Ind. Hyg.* 7, 273-89 (1925).—The method described is capable of detg. 0.1-0.5 mg. of Zn with an accuracy of 10%. The org. material was ashed at a low heat, the ash extd. with 1 cc. of 6 N  $HCl$ . After oxidation with Br, the soln. was treated with  $NaOAc$  or  $NH_4OAc$  until neutral to methyl orange and filtered. The ppt. was dissolved in acid and reprecip. to make sure all Zn was removed. 0.5 mg. of Cu was added as acetate and  $H_2S$  introduced to ppt.  $CuS$  and  $ZnS$ . The ppt. was dissolved in 0.2-0.5 cc. of 6 N  $HNO_3$  and evaporated with  $HCl$ . The Cu was pptd. in dil.  $HCl$  soln. and in the filtrate the Zn detd. colorimetrically by the urobilin test. W. T. H.

The titration of mercury with potassium cyanide and K. Jellinek's "Titration of slightly ionized acids." K. RUFF, W. WEGNER AND P. MAIUS, *Z. anorg. allgem. Chem.* 144, 313-8(1925).—Exptl. evidence is given showing that the reaction  $\text{HgCl}_2 + 2\text{KCN} = \text{Hg}(\text{CN})_2 + 2\text{KCl}$  takes place quantitatively and can be followed by means of methyl orange, which turns yellow as soon as an excess of KCN is present. The fact that Jellinek found an error of about 3% in this titration is probably due to the fact that the KCN was not pure. Thus a sample of KCN which tested 98.32% pure by argentometric titration and 98.6% pure by acidimetric titration gave excellent values with  $\text{HgCl}_2$  but another sample which tested 91.2% pure by the former method and 96.2% pure by the latter, gave results about 3% away from the truth. With pure KCN the 2 methods of analysis should give practically identical results. On the other hand, J. has claimed to be able to det. certain metals by titration of their arsenates. It is shown that such titrations are inaccurate because of hydrolytic decompn.

W. T. H.

Separation of small quantities of calcium from large quantities of magnesium. BACH, *Chem.-Ztg.* 49, 514(1925).—In the usual directions for sepn. Ca and Mg by means of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  the requisite quantities of  $\text{NH}_4\text{Cl}$  and of oxalate are usually specified very indefinitely. If the quantity of  $\text{NH}_4\text{Cl}$  is small or the excess of oxalate large, the sepn. is very unsatisfactory and for this reason several chemists have recently claimed that the method is useless. If, however, 1 g. of  $\text{NH}_4\text{Cl}$  is present, 0.8 mg. of Ca can be sepd. from 85 mg. of Mg provided not more than 100 mg. of oxalate crystals is used and there is no pptn. of  $\text{MgC}_2\text{O}_4$  if more oxalate is used in the presence of 10 g. of  $\text{NH}_4\text{Cl}$ .

W. T. H.

Use of potassium ferrocyanide in gravimetric analysis. G. LUFF, *Chem.-Ztg.* 49, 513-4(1925).— $\text{K}_4\text{Fe}(\text{CN})_6$  has not been used much as a precipitant in gravimetric analysis, although it gives pptn. with Cd, Cu, Zn, Ni, Co, Cr and Mg ions, because the pptn. are likely to be gelatinous and the reagent undergoes slight decompn. when heated with  $\text{NH}_4$  salt. These difficulties can be overcome by adding  $\text{NH}_4$  salt to make the ppt. filterable and an excess of  $\text{NH}_4\text{OH}$  to prevent the decompn. Thus good results were obtained in detg. 0.01-0.2 g. of Cd in 100 cc. of soln. by pptg. with a slight excess of powd.  $\text{K}_4\text{Fe}(\text{CN})_6$  in a soln. contg. 10 g. of  $\text{NH}_4\text{Cl}$  and 20 cc. of concd.  $\text{NH}_4\text{OH}$ . The pptn. takes place advantageously at about 75° and the ppt. can be filtered after 4 hrs. Washing with cold 2.5%  $\text{NH}_4\text{OH}$  is recommended.

W. T. H.

Gold and silver precipitation by means of metal sulfides. An analytical method. A. STEIGMANN, *Chem.-Ztg.* 49, 424(1925).—A test of the completeness of removal of Ag and Au from soln., from which these elements had been pptd. by means of metallic sulfides, is described. The new method is based upon a photographic process known as "physical development." The minute traces of Au and Ag are reduced to colloidal particles by means of  $\text{H}_2\text{O}_2$ . Upon these Au and Ag particles Ag is pptd. by means of a Lumière intensifier, which is a soln. of  $\text{AgNO}_3$ ,  $\text{Na}_2\text{SO}_4$ , and metol. The distribution of the resulting Ag crystals indicates the no. of Au or Ag nuclei present in the original soln.

J. F. ROSS

A new spectroscopic and colorimetric method for the detection and immediate determination of cobalt. G. DUNIGES, *Compt. rend.* 180, 1748-50(1925).—If as little as 0.01 mg. of Co is present per cc. of soln., 0.1 cc. of the latter mixed with 5 cc. of concd.  $\text{HCl}$  gives a blue color and the soln. shows characteristic absorption bands when viewed with a direct-vision spectroscope. By photographing the spectrum or by comparing the depths of color it is possible to det. the Co content with little difficulty. Other ions giving colored chlorides interfere somewhat with the test. If a little  $\text{SnCl}_2$  is added to the soln., the interference of  $\text{Cu}^{++}$  and  $\text{Fe}^{+++}$  is prevented. The reaction is useful for the detection of Co in Ni salts.

W. T. H.

Determination of carbon dioxide and carbon monoxide. P. LEBEAU AND P. MARASSE, *Compt. rend.* 180, 1817-50(1925).—At the temp. of liquid air,  $\text{CO}_2$  has no appreciable vapor tension so that by cooling the gas to this temp. all  $\text{CO}_2$  can be removed. By passing the gas over  $\text{I}_2\text{O}_5$  at 150° any CO present is oxidized to  $\text{CO}_2$  and can be removed by cooling again. The results of several tests are given to show the accuracy of this method of analysis for the detn. of CO and  $\text{CO}_2$  in such gases as cont.  $\text{H}_2$ .

W. T. H.

Determination of carbon monoxide by the blood method and notes on the absorption of this gas by hemoglobin in the absence of oxygen. M. NICLOUX, *Compt. rend.* 180, 1750-3(1925).—By means of a slightly modified technic it has been found possible to increase the sensitiveness of the hemoglobin method for the detn. of CO. Six cc. of blood diluted to 2% suffices for the fixation of about 0.02 g. of CO. By passing 500 cc. of air contg. 1 CO per 1000 of air through the diluted blood, it is possible to see the

2 absorption bands and only 130 cc. of air is needed if 5 parts of CO are present in 100,000 of air. According to Haldane and the English school, 1 part of CO is equiv. to 220-250 of O<sub>2</sub> in the hemoglobin reaction and under 10 mm. pressure 30% of O<sub>2</sub> will combine with hemoglobin in the absence of CO. If, from this, the necessary CO tension is computed which is required to expel O<sub>2</sub> from its combination with hemoglobin, the value 0.04 mm. of Hg will be obtained. The results of the expts. here described show that only about 1/15 as much CO is actually required.

W. T. H

Critical examination of the determination of silica in ores, slags, furnace additions and refractory materials. A STADELER. *Stahl u. Eisen* 44, 1477-81 (1924); *Z. angew. Chem.* 38, 330 (1925).—A comprehensive study of various methods served to corroborate the results of the work of W. F. Hillebrand.

A. HUNDELMANN

Proposed tentative methods of chemical analysis of ferro-alloys. ANON. *Proc. Am. Soc. Testing Materials* No. 13s, 1-33, preprint (June, 1925).—*Detn. of Si in Fe-Si*. The proposed method calls for fusion of 0.5 g. of finely powdered sample with Na<sub>2</sub>O<sub>2</sub> in an Fe crucible, extn. of the melt with water and detn. of SiO<sub>2</sub> in the aq. ext. after the usual dehydration with HCl. *Detn. of Mn in Fe-Mn*. The proposed method is a modification of the well-known NaBiO<sub>3</sub> method. It calls for soln. of 0.25 g. of powder in concd. HNO<sub>3</sub> or, if this is unsuccessful, fusion of the residue with soda and addition of the HNO<sub>3</sub> soln. of the melt to that obtained with acid alone. The soln. is evapd. to fumes with H<sub>2</sub>SO<sub>4</sub> and, after diln. with 200 cc. of 30% HNO<sub>3</sub>, the usual procedure is followed except that the wts. of NaBiO<sub>3</sub> and of FeSO<sub>4</sub> used are large. *Detn. of P in Fe-Si*. The method is an adaptation of the well known Handy method and calls for pptn. of phosphomolybdate and alkalimetric titration of the ppt. *Detn. of Si in Fe-Mn*. The Drown method is recommended. *Detn. of Cr in Fe-Cr*. The method consists in fusing with Na<sub>2</sub>O<sub>2</sub>, extg. with water, reducing the Na<sub>2</sub>CrO<sub>4</sub> with Fe<sup>++</sup> and finally titrating the excess with KMnO<sub>4</sub>. *Detn. of V in Fe-V*. The sample is dissolved in nitro sulfuric acid and after fuming, the dil. soln. is oxidized with KMnO<sub>4</sub>. A slight excess of Fe<sup>++</sup> is added and the excess removed by treatment with (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. Finally the V is titrated with KMnO<sub>4</sub>. *Detn. of P in Fe-V*. The metal is treated with HNO<sub>3</sub> and HF in a Pt dish and HF removed by evapn. with more HNO<sub>3</sub>. The P is pptd. as phosphomolybdate with V in the quadrivalent condition. The yellow ppt. is dissolved in NH<sub>4</sub>OH and, after addn. of citric acid, the P is obtained as MgNH<sub>4</sub>PO<sub>4</sub>. The ppt. is purified and any As and V removed prior to a final pptn. as MgNH<sub>4</sub>PO<sub>4</sub>. *Detn. of S in Fe-V*. After dissolution in HNO<sub>3</sub>, HCl is added and the soln. evapd. repeatedly to dryness. Finally in a properly diluted soln., the S is pptd. as BaSO<sub>4</sub> and the ppt. carefully digested with acid to remove all V. *Detn. of Si in Fe-V*. If less than 4% of Si is present the method recommended is essentially the Drown method. Otherwise it is necessary to fuse with Na<sub>2</sub>O<sub>2</sub> at the start and then the use of H<sub>2</sub>SO<sub>4</sub> alone is recommended for making the soln. acid and dehydrating. *Detn. of Al in Fe-V*. After the metal is dissolved in HNO<sub>3</sub>, the soln. is evapd. repeatedly with HCl until a small vol. of concd. HCl soln. is obtained. To this ether and HCl gas are added and the insol. AlCl<sub>3</sub> is filtered off. The ppt. is dissolved in dil. HCl and the pptn. repeated in order to insure a pure ppt. This is dissolved in dil. HCl and pptd. with NH<sub>4</sub>OH for the usual detn. as Al<sub>2</sub>O<sub>3</sub>. *Detn. of W in Fe-W*. After the removal of Si by treatment with HF and H<sub>2</sub>SO<sub>4</sub>, the tungstic acid is pptd. in the usual way by digestion with dil. HCl and cinchonine hydrochloride. The ppt. is ignited carefully and examd. for impurities by fusing with soda and weighing the residue that is then insol. in water. *Detn. of P in Fe-W*. After treatment with HNO<sub>3</sub> and HF in a Pt dish, the soln. is treated with KMnO<sub>4</sub> and evapd. H<sub>2</sub>SO<sub>4</sub> is added and HF removed by evapn. After dilg. with water, the excess KMnO<sub>4</sub> is removed by H<sub>2</sub>SO<sub>4</sub> and a ppt. of MgNH<sub>4</sub>PO<sub>4</sub> is obtained in ammoniacal citrate soln. The ppt. is dissolved in HCl, As removed by boiling with KBr and the P pptd. as phosphomolybdate under the usual conditions. The yellow ppt. is analyzed by the Handy method. *Detn. of S and Si in Fe-W*. For the S detn. the sample is fused with soda and niter in a Pt crucible and the melt extd. with water. Si and W are removed by evapn. and dehydration and finally the S is pptd. as BaSO<sub>4</sub> in dil. HCl soln. In the above treatment the residue of WO<sub>3</sub> contains most of the Si and the residue from the original fusion contains the rest. The former is digested with acid to remove all sol. Na salts and the latter is treated with acid and SiO<sub>2</sub> obtained after the usual dehydration. The SiO<sub>2</sub> and WO<sub>3</sub> are weighed together and the SiO<sub>2</sub> is obtained by volatilization as SiF<sub>4</sub> in the usual way. *Detn. of Sn, Bi, Sb and Cu in Fe-V*. Two methods are suggested, the first calling for soln. in acid and the second calling for an initial fusion. Possibly Sn is partially lost as in the former case because HF is used and unless removed it interferes with the pptn. of Sn sulfide. In the acid method, the metal is digested with HNO<sub>3</sub> and HF as in the W detn. and the soln. evapd. with H<sub>2</sub>SO<sub>4</sub>.

Water and HCl are added and considerable tartaric acid. Enough  $\text{NH}_4\text{OH}$  is added to make the  $\text{WO}_3$  dissolve but without making the soln. alk. In the fusion method the sample is fused with  $\text{Na}_2\text{O}_2$  and the melt extrd. with HCl and considerable tartaric acid. In either case, the Bi, Cu, Sb and Sn are pptd. by means of  $\text{H}_2\text{S}$ , the sulfides dissolved in HCl and  $\text{KClO}_3$  and pptd. a second time in the presence of tartaric acid; in this way a ppt free from W is obtained. The sulfide ppt. is digested with KOH and  $\text{K}_2\text{S}$  soln. to sep. Bi and Cu from Sb and Sn. The sulfide ppt. is dissolved in  $\text{HNO}_3$  and the Bi pptd. as basic carbonate and weighed as  $\text{Bi}_2\text{O}_3$ . In the filtrate from the Bi, the Cu is pptd. as  $\text{CuS}$  and weighed as  $\text{CuO}$ . From the above mentioned alkaline sulfide soln. the Sb, As and Mo are obtained as sulfides after pouring the soln. into oxalic acid and ammonium oxalate soln. and pptg. as with  $\text{H}_2\text{S}$ . In the filtrate from this pptn. the Sn is pptd. as sulfide after adding  $\text{NH}_4\text{OH}$  and  $\text{H}_2\text{S}$ . The sulfide is ignited to  $\text{SnO}_2$  and the oxide fused with  $\text{Na}_2\text{O}_2$ . The melt is treated with HCl and the Sn reduced by Ni to the bivalent condition and titrated with  $\text{I}_2$ . The Sb is detd. in the above-mentioned sulfide ppt. by dissolving in HCl and Br. It is assumed that any As is removed as  $\text{AsCl}_3$  by evapg. with concd. HCl. Then after dilg.  $\text{HNO}_3$  is added to oxidize any Fe, this is pptd. by adding  $\text{NH}_4\text{OH}$  and it is assumed that the Fe ppt. will carry down all Sb. The Mo all passes into the filtrate. The Fe-Sb ppt. produced by  $\text{NH}_4\text{OH}$  is dissolved with HCl tartaric acid mixt. and the Fe reduced with  $\text{NH}_4\text{HSO}_3$ . After boiling off  $\text{SO}_2$ , the Sb is again pptd. as sulfide and after suitable ignition weighed as  $\text{Sb}_2\text{O}_3$ . For the As detn. it is recommended to fuse a fresh sample of Fe-W with soda and niter and leach with water. The soln. and residue is poured into dil.  $\text{H}_2\text{SO}_4$  and the As pptd. by  $\text{NH}_4\text{OH}$  as  $\text{FeAsO}_4$ , with addn. of Fe if necessary. The ppt. is dissolved in  $\text{H}_2\text{SO}_4$  and after the removal of every trace of nitrate, the As is volatilized as  $\text{AsCl}_3$  by adding concd. HCl and  $\text{FeSO}_4$  and distg. The distillate is collected in water and from it As is pptd. as  $\text{As}_2\text{S}_3$ , in which form it is weighed after suitable treatment. Criticisms of these tentative methods are solicited and should be directed to Chas. McKnight, Jr., 67 Wall St., New York City.

W. T. H.

Methods for determining manganese in quality steels with particular attention to the silver-nitrate-persulfate method. A. KROFF, *Chem.-Ztg.* 49, 517-20 (1925).—The elements W, Cr, Mo, V and Co interfere with the direct detn. of Mn in alloy steels. The Volhard method, involving treatment with  $\text{ZnO}$ , takes care of most all these elements but careful study of the simpler persulfate method has shown how it also can be modified to make it apply to the analysis of all steels. Alkali persulfate reacts with various cations to form peroxides. When added to a soln. of pure  $\text{Mn}^{++}$  salt, it causes pptn. of  $\text{MnO}_2$  but if sufficient  $\text{Ag}^+$  is present in the soln. no pptn. of  $\text{MnO}_2$  results but all of the Mn is converted into  $\text{MnO}_4^-$ . The cause for this catalytic effect of the  $\text{Ag}^+$  is traced to the formation of Ag peroxide, formed more rapidly than is  $\text{MnO}_2$ , and it reacts, in  $\text{HNO}_3$  or  $\text{H}_2\text{SO}_4$  solns., with  $\text{Mn}^{++}$  in the same way that  $\text{PbO}_2$  and  $\text{Bi}_2\text{O}_3$  do. The cause for low results in the persulfate method is not usually an incomplete oxidation of the  $\text{Mn}^{++}$  to  $\text{MnO}_4^-$  but rather to a subsequent decompn. of the  $\text{MnO}_4^-$ . If the conditions are properly maintained so as to avoid this decompn., the method is perfectly satisfactory as far as the oxidation of the  $\text{Mn}^{++}$  goes. It is customary to titrate the  $\text{MnO}_4^-$  by means of a standard arsenite soln. Under the conditions that have hitherto prevailed in most procedures, the oxidation of the As from the trivalent to quinquevalent condition was complete but the reduction of the  $\text{MnO}_4^-$  has yielded a green soln. contg. a part, at least, of the Mn in the trivalent condition. Because of the indefiniteness in the reduction of the  $\text{MnO}_4^-$  in the final titration with arsenite, it has been necessary to use an empirical value for the reducing power of the arsenite soln. and for this reason the method has not been satisfactory from a theoretical standpoint. This difficulty, however, can be overcome by adding a certain amt. of HCl to the  $\text{MnO}_4^-$  soln. just before titrating with arsenite. In HCl soln. salts contg. Mn with a valence greater than 2 are not stable and are easily reduced to the bivalent condition. The following procedure takes these points into consideration. Dissolve 1-2 g. of steel in 30-50 cc. of 9 N  $\text{H}_2\text{SO}_4$  and oxidize the  $\text{Fe}^{++}$  by dropwise addn. of concd.  $\text{HNO}_3$ . Cool, dil. in a measuring flask and use an aliquot contg. 0.1-0.2 g. of the original sample. Dil. this to 150 cc. in a 300-cc. Erlenmeyer flask and add 10-20 cc. of 9 N  $\text{H}_2\text{SO}_4$ . Heat to boiling and introduce 10-20 cc. of 0.01 N  $\text{AgNO}_3$  soln. and 10 cc. of 10%  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  soln. Boil 3 mins., cool under the tap, add 10 cc. of 6 N HCl and at once titrate with standard arsenite soln.

W. T. H.

Determination of arsenic in steel. A. E. CAMERON, *Ind. Eng. Chem.* 17, 856-7 (1925).—The  $\text{HNO}_3$  soln. obtained by treating 5 g. of steel in an excess of 6 N  $\text{HNO}_3$  is evapd. to dryness and baked till all nitrate is decomposed. The residue is taken up in 100-150 cc. of concd. HCl and after the addn. of 20 g.  $\text{Cu}_2\text{Cl}_2$  the As is removed as

AsCl<sub>3</sub> by distn. The distillate is collected in water. The resulting soln. is neutralized and the As detd. iodometrically. W. T. H.

Permanent standards as a possible source of error in iron determinations. E. S. HOPKINS *Ind Eng Chem*, 17, 832(1925).—The colorimetric value of Co platinum standards as given in Standard Methods of Water Analysis (Am. Pub. Health Assoc.) should be regarded as merely approximations and these solns. should be compared with actual Fe colors to obtain the true values. W. T. H.

Safeguarding of seals. T. R. HODGSON. *Analyst* 50, 236-7(1925).—A simple safeguard is to provide the inspector with several seals, each of which bears a secret mark not obvious by casual examn. Then the analyst is likely to know if the seal has been tampered with. W. T. H.

Estimation of phosphorus in the presence of vanadium. G. W. GRAY AND C. D. GARBUTT *Engineering* 119, 717(1925).—Treat 2 g. of finely powd. alloy, or other material, with 50 cc. of 6 N HNO<sub>3</sub>; after the reaction slackens, add 5 cc. of HCl and digest 10 mins. Evap. to dryness and remove SiO<sub>2</sub> as usual. Treat the ppt. with HF, fuse the non volatile residue with soda and yster and add the aq. ext. of the melt to the main soln. Evap. with HCl and carry out the Rothe ether sepn., getting all of the V, P and As in the aq. soln. and nearly all of the Fe in the ethereal soln. Evap. off the ether from the aq. soln., add 6 g. of citric acid and ppt. the As and P with magnesia mixt. in the usual way. The V will remain in soln. After filtering off the MgNH<sub>4</sub>PO<sub>4</sub> dissolve it in HCl and remove As by means of H<sub>2</sub>S. To the filtrate from the As<sub>2</sub>S<sub>3</sub>, add FeCl<sub>3</sub> and ppt. FePO<sub>4</sub> by means of NH<sub>4</sub>OH. Det. P in this ppt. by the usual molybdate method. W. T. H.

Artificially aged documents. O. A. MENDELSON. *Analyst* 50, 287(1925).—Lucas in his *Forensic Chemistry* states that he has never known of aging documents by means of tea or coffee. In a recently disputed will case, letters purporting to be over 60 yrs. old proved to have been treated with tea. An aq. soln. of parts carrying no writing had a pale brown color, gave a slow Fe test, was decolorized by NaClO and by evapn. with HCl and the usual subsequent treatment gave the murexide reaction, just as weak tea does. W. T. H.

Method for the identification of two organic substances. E. MUEMANN. *Oesterr. Chem. Ztg* 28, 86-7(1925).—To prove that an unknown substance is identical with something else, it is recommended to test the soly. of not more than 1 mg. of each on a small watch glass with 1-2 drops of a series of solvents, beginning with the most volatile, and always in the same sequence. Then, by distinguishing between (1) rapid soly., (2) slow but complete soly., (3) slight soly. and (4) practically insoly., it is possible to make the identification by means of these nos. arranged in a table. If there are similar isomers, there is likely to be some difficulty. Thus, with 21 solvents tried, CCl<sub>4</sub> was the only one that served to differentiate between  $\alpha$ - and  $\beta$ -naphthols and  $\alpha$ - and  $\beta$ -naphthylamines. W. T. H.

A sensitive adaptation of the iodoform reaction and the detection of acetone in spirit. I. M. KOLTSOFF *Pharm. Weekblad* 62, 652-5(1925).—When dil. EtOH (10 cc.) is treated with 100 mg. KI, 100 mg. chloramine-T and 10-20 drops of 4 N NaOH and warmed to 60°, CHI<sub>3</sub> seps. in a red amorphous form. If the mixt. is allowed to stand 1 hr. the test is sensitive to 1 part EtOH in 1000 H<sub>2</sub>O. Under the same treatment MeAc gives a yellow cryst. sepn. of CHI<sub>3</sub>, the test being sensitive to 2 per mille. If now NH<sub>4</sub>OH (10-20 drops) is used in place of NaOH, the EtOH fails to react and thus MeAc can be detected in the presence of EtOH. One part of MeAc in 10,000 parts of 10% EtOH gives a positive reaction in 2 hrs. The test is probably applicable also to MeAc in urine. A. W. DOX.

Differentiation of citric from tartaric acid. WALTER PARR. *Giorn. chim. ind. applicata* 6, 537-8(1923).—The Moehler-Denigès and the Finnera reactions afford a means of detecting small quantities of tartaric acid in presence of large quantities of citric acid, but are of no value in detecting small quantities of citric acid present in large quantities of tartaric acid. P.'s reagent consists of 3 g. NiH<sub>2</sub> phosphomolybdate and 0.3 g. NiH<sub>2</sub> vanadate dissolved in 100 cc. concd. H<sub>2</sub>SO<sub>4</sub>. On placing in this soln. a little of the substance contg. citric acid in presence of much tartaric acid, there develops an intense blue ring or color that becomes green on heating and blue again on cooling. The presence of 1% citric acid gives an intense blue color. Smaller % of citric acid gives a positive indication in the form of a blue ring, provided the substance and the reagent are not mixed during the test. Sugars interfere with the test by giving brown colors with the H<sub>2</sub>SO<sub>4</sub>. Glucose and sucrose give a greenish coloration. The presence of much alc. disturbs the reaction by giving at once and in the cold a non-reversible blue color. Reaction with cinnamic acid: in the cold a very fugitive violet

color, then red; on moderate heating turbid maroon, changing to a violet mass on cooling. With succinic acid: unchanging clear golden yellow color, still persisting on moderate warming. With malic acid: golden yellow color in the cold, slowly passing to clear green; on moderate warming the color becomes a very limpid blue, the liquid remaining clear on cooling.

ROBERT S. POSMONTIER

Detection of benzyl alcohol as dibenzyl oxalate. ALEXANDER ST. PFAU. *Perfumery Essent. Oil Rec.* 16, 190-1 (1925).—Introduce a small quantity (about 0.03 g.) of powd. anhyd.  $K_2CO_3$  into a test tube together with 10 drops of the oil fraction under examn. (more if the benzyl alc. content is less than 50%) and 10 drops of diethyl oxalate. Warm gently over a small flame, whereby the EtOH formed passes off as vapor. When the contents of the tube solidify or become yellow—after the lapse of 1 min.—cool somewhat, add about 2 cc. of  $H_2O$ , then warm gently until the solid is remelted; this dissolves out the  $K_2CO_3$ , which later might interfere. Cool the tube once more, finally in ice, whereupon the dibenzyl oxalate sets as a solid crust on the sides of the tube. Pour off the aq. liquor, add about 1 cc. of EtOH and warm to dissolve the benzyl oxalate, which on cooling again crystallizes out. Filter, wash with a little EtOH and dry on a porous plate. The m. p. of the product so obtained is usually from 79 to 80°.

W. O. E.

Micro-estimation of methoxyl. J. C. SMITH. *J. Chem. Soc.* 127, 912 (1925).—In the English translation of Pregl's book the concn. of the  $AgNO_3$  soln. recommended for his detn. is given as 200 g.  $AgNO_3$  per 200 g. alc., it should be 200 g.  $AgNO_3$  in 500 g. alc. The more concd. soln. causes low results.

W. T. H.

Study of the Höchst test for the determination of anthracene. F. H. RHOADS, M. L. NICHOLS AND C. W. MORSE. *Ind. Eng. Chem.* 17, 839-42 (1925).—The standard Höchst test is subject to error largely because of the partial oxidation of the anthracene to anthraquinone. The following modified procedure is more accurate and more rapid. Dissolve 1 g. of sample by heating with 45 cc. of AcOH under a reflux condenser. To the boiling soln. add  $CrO_3$  (dissolved  $1\frac{1}{2}$  its wt. of AcOH) until a permanent brown color is obtained. Boil gently 2 hrs. longer. Cool in the air for 15 mins. and then in ice water for the same time. After 30 mins. more, filter, wash with hot water till a colorless filtrate is obtained, then with 500 cc. of hot 1% NaOH and then with 500 cc. of hot water. Transfer to a flat-bottomed dish, dry in a steam bath and heat on the bath for 10 mins. with 10 cc. oleum contg. 10%  $SO_3$ . Allow to stand over hot water for 12 hrs. in a desiccator. Add 200 cc. of water, filter and wash with water, dil. NaOH, etc., as above. Dry to const. wt. at 110° and weigh. Sublime the anthraquinone by heating 30 mins. at 350° and weigh the residue. To the loss in wt. add 0.4 mg. and multiply by 0.8558 to det. the wt. of anthracene in the original sample.

W. T. H.

Rapid method of analyzing xanthate. W. HIRSCHKIND. *Eng. Mining J.-Press* 119, 968-70 (1925).—Test for sulfide.—Dissolve 1 g. in 100 cc. of cold water and test with a little Na nitroprusside. Test for thiocarbonate.—If the ppt. which forms immediately on adding a little 10%  $Pb(OAc)_2$  to 50 cc. of 2% xanthate soln. has a red or brown color, thiocarbonate is indicated. Available xanthate.—Dissolve 7.5 g. of xanthate in 50 cc. of cold water and rinse the soln. into a 250-cc. measuring flask. Add 10-20 cc. of 10%  $BaCl_2$  soln., shake, make up to the mark and filter. To 25 cc. of the filtrate add phenolphthalein and titrate any free caustic alkali with 0.1 N acid. To another 25 cc. of filtrate add 50 cc. of the standard acid while stirring and allow the soln. to stand 10 mins. The acid liberates xanthic acid, which decomposes into  $CS_2$  and alc., so that the acid consumed is a measure of the xanthate. Add methyl red indicator and titrate the excess acid. In the computation, allow for any original alkalinity. Methods for the detn. of thiosulfate, sulfites, carbonates, etc., are indicated and correspond to standard procedure.

W. T. HALL

Detection of organic cyanogen compounds in "alliol." LOUIS DESVERGNES. *Ann. chim. anal. chim. appl.* 7, 129-30 (1925).—The name "alliol" is given to impure sulfides of C obtained in the "heads" from the distn. of light oils. The cyanogen present may exist as RCN, RNC, ROCN, RNSC or RCSN. The following tests are recommended: (1) Test for nitriles.—The method is based on the reaction  $RCN + 2H_2 = RCH_2NH_2$ . Treat 50 cc. of alliol with 5 g. of Na and 50 cc. of alc. under an upright condenser. Collect the evolved gas in dil. HCl. Two layers are obtained. Test the upper aq. layer for amine with 0.7% picric acid soln. If the test is positive test the original sample for amine in the same way. (2) Test for carbamides.—The test depends upon the reaction  $RNC + 2H_2O = RNH_2 + HCOOH$ . Digest in the same kind of an app. as that used above, 50 cc. of alliol with 50 cc. of 6 N HCl. Collect the distillate in dil. acid. Test for amine as in (1). (3) Test for isocyanate.—The test is based on the reaction  $RCON + 2KOH = RNH_2 + K_2CO_3$ . Heat, as above, 50 cc. of alliol

with 25 cc. of alcoholic KOH and test the distillate for amine. (4) *Test for thiocyanate esters*—The test is based on the reaction  $\text{RNCS} + \text{H}_2 = \text{HCN} + \text{RSH}$ . In the same app. treat 50 cc. of alcoh. with 50 cc. of 10%  $\text{H}_2\text{SO}_4$  and 5 g. of powdered Zn and collect the distillate in dil. NaOH. (5) *Test for isothiocyanate esters*—The test is based on the reaction,  $\text{RSCN} + 2\text{H}_2\text{O} = \text{CO}_2 + \text{H}_2\text{S} + \text{RNH}_2$ . Heat in the same way, 50 cc. of alcoh. with an equal vol. of 6 N HCl and collect the evolved gas in  $\text{Ba}(\text{OH})_2$ . W. T. H.

**Analysis of mixtures of sugars.** E. HILDT. *Ann. chim. anal. chim. appl.* 7, 4-8 (1925).—Interesting data are given concerning the hydrolysis of different sugars by treating with dil. acid at different temps. and for different periods. It is pointed out, in particular, how much in error the degree of inversion may be if detd. by the polaroscope rather than by means of Fehling soln. W. T. H.

**Influence of hydrogen-ion concentration on the colorimetric determination of pyrogallol and catechol derivatives.** S. GLASSSTONE. *Analyst* 50, 49-53 (1925).—Mitchell (C. 17, 1401) and later Miss Price (C. A. 19, 623) have worked with a colorimetric method for the detn. of pyrogallol and catechol derivs. which depends on the formation of a reddish violet color on the addition of  $\text{FeSO}_4$  Rochelle salt to a very dil. soln. The work here described shows that different substances of the class in question have different H-ion concn. within which the violet color is formed to the best advantage and unless precautions are taken to maintain the proper H-ion concn., 2 solns. with equal content of pyrogallol or catechol nucleus may not give the same intensity of color in the test. Thus with the following substances the color was produced within these pH limits, pyrogallol 6.5-10.3, gallic acid 5.9-10.3, tannic acid 4.1-11.1, catechol 7.0-10.3, pyrocatechuic acid 6.3-10.4. In applying the test to pyrogallol derivs. it is best to modify the reagent by adding  $\text{NH}_4\text{OAc}$  soln. to act as a buffer salt and with catechol a few drops of  $\text{NH}_4\text{OH}$  should be used. W. T. H.

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**Reagent for use as a substitute for Fehling solution.** G. J. VAN ZOEERREY and E. J. De Free. U. S. 1,543,961, June 30. A reagent in dry form (for use after addn. of  $\text{H}_2\text{O}$ ) is formed of  $\text{CuSO}_4$ , K tartrate and  $\text{LiOH}$ .

## S—MINERALOGICAL AND GEOLOGICAL CHEMISTRY

EDGAR T. WHEELEY

**X-ray investigation of the crystal structures of pyrrhotite, breithauptite, pentlandite, millerite, and related compounds.** N. S. ALLEN. *Geol. For. Fork* 47, 19-72 (1925).—Natural crystals and artificial products were examd. by 3 different X-ray methods. Pyrrhotite, troilite, and breithauptite have the space group  $D_{6h}^4$ , with 2 mols. in the elementary parallelepiped. Artificial  $\text{FeSe}$ ,  $\text{NiS}$ ,  $\text{NiSe}$ ,  $\text{CoS}$ , and their mixed crystals,  $\text{FeS}$ , and  $\text{FeS} + \text{S}$  have the pyrrhotite structure. In pyrrhotite  $c$  decreases as the S content increases, and it is apparently a solid soln. of S in  $\text{FeS}$ , in which S atoms replace Fe atoms. For pyrrhotite:  $a = 3.43 \text{ \AA}$ ;  $c = 5.68$ ,  $c/a = 1.66$ ; breithauptite: 3.9, 5.1, 1.31. Pentlandite has a face-centered cube with edge 10.0  $\text{\AA}$ .  $U'$ , containing 32 S atoms and an equal no. of Ni + Fe atoms; space group probably  $O_h^1$ . Millerite belongs to space group  $C_{2v}^1$ , with 3 mols. in each elementary cell, the edge of the elementary rhombohedron being 5.54  $\text{\AA}$ .  $U'$ , the pole-edge-angle  $116.7^\circ$ . E. T. WHEELEY.

**The crystal structure of dolomite.** J. A. WASASTJERNA. *Soc. Sci. Fennica Comm. Phys.-Math.* 2, No. 14, 16 pp. (1925).—An investigation both by the powder method and spectrometric examn. of (100) and (111) showed that dolomite has a rhombohedral elementary cell containing one mol. of  $\text{CaMgC}_2\text{O}_6$ . The length of the side is  $5.94 \times 10^{-8} \text{ cm}$ ; the angle between the axes is  $47^\circ 20'$ . The space group is  $C_{2v}^2$ . E. T. H.

Optical determinations on  $\text{FeCO}_3$ ,  $\text{MnCO}_3$ , and  $\text{CaMg}(\text{CO}_3)_2$ . N. SUNDIUS. *Geol. For. Forh.* 47, 269-70 (1925).—The data given are

	$\text{FeCO}_3$	$\text{MnCO}_3$	$\text{MgCO}_3$	$\text{CaCO}_3$	sp. gr.	$n_D$	$n_P$	Cleavage angle
Dolomite, Taberg, Sweden	3.96	1.42	43.70	51.02	2.900	1.688	1.508	73°18'
Siderite, Ivigtut, Greenland	91.80	1.63	0.12	0.14	3.927	1.873	1.633	73°3'
Rhodochrosite, Alma, Colo.	1.60	97.83	0.58		3.691	1.816	1.600	73°2'

H. F. H.

The thermal decomposition of siderite, manganese spar and dolomite. J. A. HEDVALL. *Geol. For. Forh.* 47, 73-80 (1925).—Two methods were used: (1) about 0.5 g. of the finely powdered sample was heated in an electric oven. Temp. readings were taken every 10 sec. by means of a Pt-PtRh element; (2) about 0.5 g. of finely powdered sample was heated in a tube, the metal cover of which was cemented with plaster of Paris. A rapid stream of N. free from  $\text{CO}_2$ , was passed through in carry off the  $\text{CO}_2$ , which was taken up by  $\text{Ba}(\text{OH})_2$  soln. in another tube. The sample was heated slowly and a thermometer showed at what temp. the first trace of  $\text{CO}_2$  came off. Dissociation of siderite begins at about 195° and is complete at about 490°. 1.5 g. siderite lost all its  $\text{CO}_2$  between 190° and 500° in 15 mins. Dissociation of  $\text{MnCO}_3$  begins at about 395° and is complete at about 575°; 0.5 g.  $\text{MnCO}_3$  lost all its  $\text{CO}_2$  between 395° and 575° in 110 mins. Dissociation of dolomite begins at about 540° and is complete at about 910°. The evolution of  $\text{CO}_2$  is irregular and there is evidence that free  $\text{CaCO}_3$  is present, formed perhaps according to  $\text{CaO} + \text{MgCa}(\text{CO}_3)_2 = 2\text{CaCO}_3 + \text{MgO}$ . The probability that dolomite is a mixt., a double salt or a solid soln. is discussed. W. SEGERSTROM.

Some artificial mineral compounds. P. J. HOLMQUIST. *Geol. For. Forh.* 47, 112-4 (1925).—Quartz bricks in a Martin furnace undergo changes in chem. compn. at high temp. Notchlike amts. of Fe are taken up. About 2% of the Ca content is lost. Under the slag are found small, dull yellow, rhombododecahedral crystals of melanite. Tridymite, cristobalite, magnetite and an undetd. slag silicate rich in Fe were also found. A deposit of magnetite in a Platen-Munter cooler (using  $\text{NH}_3$  and  $\text{H}_2\text{O}$  at 10 atm. and 110°) was investigated. In the 6-mm. Fe tube, where the  $\text{NH}_3$  was most rapidly evolved from the liquid, octahedral crystals of magnetite were found. Where the  $\text{NH}_3$  was evolved more slowly the crystals were smaller. A sort like powder of magnetite was found throughout the whole interior. The magnetite is carried as such in the  $\text{NH}_3$  soln., from which it separates by direct crystn. Fe wire briquets were subjected to elec. arc flame. The easily flowing melt on cooling crystal. as magnetite, coated by oxidation in air with a thin layer of hematite which at high temp. formed a twinned laminated variety. Two forms of crystal  $\text{Fe}_3\text{O}_4$  exist—a high temp. ( $\beta$ -) and a low temp. ( $\alpha$ -) form. W. SEGERSTROM.

Ferroplumbite from Jacobsberg. G. AMINOFF. *Geol. For. Forh.* 47, 266-8 (1925).—Notes by the late H. Sjögren found in the Royal Museum show the analysis of grains, 1 mm. in size, sp. gr. 5.98, easily sol. in warm concd.  $\text{HCl}$  and warm 40%  $\text{H}_2\text{SO}_4$  to be:  $\text{Fe}_2\text{O}_3$  63.66,  $\text{FeO}$  0.67,  $\text{MnO}$  1.13,  $\text{PbO}$  32.30,  $\text{CaO}$  0.43,  $\text{MgO}$  0.65,  $\text{H}_2\text{O}$  0.32, insol. 0.39, Cu (native) 0.24,  $\text{Ti}_2\text{O}_3$  (?) 0.09, sum 99.88%. Another portion carefully sampled and freed from magnetic impurities was analyzed, the Cu, Ti and insol. parts deducted, and the results recalcd. to 100, giving:  $\text{Fe}_2\text{O}_3$  63.53,  $\text{FeO}$  0.70,  $\text{MnO}$  1.55,  $\text{PbO}$  32.65,  $\text{CaO}$  0.39,  $\text{MgO}$  0.88,  $\text{H}_2\text{O}$  0.30, sum 100.00%. This appears to be a new mineral, with the probable formula  $\text{PbO} \cdot 2\text{Fe}_2\text{O}_3$ , the name referring to the compn. W. SEGERSTROM.

The labradorization of the feldspars. O. B. BJORNDAL. *Det. Kgl. Danske Vidensk. Selskab, Math.-fys. Medd.* 6, No. 3, 3-79 (1921).—Labradorization is the reflection of light from submicroscopic planes, which usually have but one orientation for a given specimen. The planes never have a position capable of expression by simple indices. Aventurization is entirely different (cf. Andersen, *C. A.* 9, 3192). B. examd. 53 specimens of feldspars showing this phenomenon. Only certain varieties have labradorization: orthoclase contg.  $\text{OrAb}$ , to  $\text{Or}_2\text{Ab}_2$ ; albite-oligoclase with 8-14%  $\text{An}$ ; and labradorite with 38-49%  $\text{Ab}$ . In orthoclase the labradorization is caused by intergrown lamellae of albite, at 72-75° to (001) in the zone of the orthoclases. In the plagioclases there are 4 different orientations of the planes of labradorization, but the effect is generally visible through (010). In the plagioclases the cause is unknown. F. F. H.

New mineral analyses. H. DITTLER. *Min. Petr. Mitt.* 36, 213-6 (1924).—Talc from Sirvan, Armenia—A compact, pale yellowish green mineral, thought to be

"agalmatolite," gave d 2.832,  $n$  1.554, and, on material dried at 110°, the results under I. The mol ratios  $H_2O : RO : SiO_2 = 1:2.5:3$  differ somewhat from those of talc.

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MnO	NaO	MgO	CaO	H <sub>2</sub> O	Sum
I	59.44	0.24	trace	1.51	0.12	0.02	31.11	1.85	5.80	100.09

*Damourite from Mt. Lyell, Tasmania*.—Pale greenish material translucent at the edges and consisting of a compact aggregate of fine scales has d. 2.872; from analysis II (mean of 2) is calcd. muscovite ( $KH_2Al_2Si_2O_6$ ) 98.07, fayalite ( $Fe_2SiO_4$ ) 1.93 mol.-%. *Feldspars from Loser Austria*.—These are from a feldspar quarry in pegmatite between Krems and Gfohl. Microcline perthite, d. 2.553, showing enclosed spindles of albite, gave III, corresponding with orthoclase 68.10, albite 31.90 mol.-%. Albite, d. 2.625, as bluish white cleavages, gave IV, corresponding with albite 98.14, orthoclase 1.86 mol.-%.

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	CaO	K <sub>2</sub> O	NaO	H <sub>2</sub> O (-110°)	H <sub>2</sub> O (+110°)	Sum
II	43.37	39.03	0.40	1.41	...	10.98	0.75	0.76	3.80	100.50
III	64.20	20.55	0.14	...	trace	11.26	3.48	...	0.28	99.91
IV	66.80	20.94	...	...	trace	0.34	11.91	...	0.10	100.09

B. C. A.

*Phengite from certain mountain rocks*. T. DU RIETZ. *Geol. För. Förh.* 46, 712-4 (1924).—Muscovite from Västerbotten shows in polished samples  $2V_0 = 54^\circ 20'$  instead of  $69^\circ$  usually found in phengite. Other samples gave  $2E = 51^\circ$  and  $52^\circ$  by the Malard-Becke method.

W. SEGERBLOM

*Hisingerite from Blaine Co., Idaho*. D. F. HEWITT AND W. T. SCHALLER. *Am. J. Sci.* 10, 29-38 (1923).—Hisingerite occurs in several mines, where it has resulted from the alteration of siderite at 200 to 450 ft. below water level and the lower limit of weathering. It was probably formed by the action of hot spring waters which also deposited zeolites in fractures in the wall rocks. The mineral is dark brown, conchoidal fracture, vitreous to greasy luster, hardness 3-3.5, streak light brown. Material from the Bellevue King mine rapidly changes color from claret-red to dark brown on exposure. It is wholly isotropic,  $n$  1.57 in 1914, when analyzed, but in 1924 it was 1.44. Analysis gave:  $SiO_2$  38.14,  $Fe_2O_3$  36.66,  $FeO$  0.84,  $MgO$  2.45,  $MnO$  trace,  $CaO$ ,  $P_2O_5$ ,  $SO_3$  and  $CO_2$ , none,  $H_2O + 8.53$ ;  $H_2O - 13.20$ , sum 99.92%. That from the Minnie Moore mine is partly isotropic with  $n$  1.66 constant from 1914 to 1924; partly birefringent, with very small  $2V$ . It contained  $Fe_2O_3$ ,  $SiO_2$ , and  $H_2O$ . The interpretation of amorphous hisingerite, with its variable properties, is at present impossible.

E. F. H.

*A new find of dixerite at Långban mine*. G. FLINKE. *Geol. För. Förh.* 47, 203-14 (1925); cf. C. A. 18, 366, 2306.—Dixerite is accompanied by hematite, mica, no. 138, heavy spar, calcspar, tulasite, pyroaurite, no. 278, allaktite and some other minerals not yet detd. Five distinct types of dixerite occur at Långban; the crystal habits of these are described in detail.

W. SEGERBLOM

*Svabite from Långban, a mineral new for this place*. G. FLINKE. *Geol. För. Förh.* 47, 127-34 (1925).—This was listed (see C. A. 18, 2306) as "Långban mineral no. 189, apatite like, colorless, well-formed crystals in calcite." The crystals belong to the pyramidal hemihedral class of the hexagonal system;  $m(10\bar{1}0)$ ,  $c(0001)$ ,  $x(10\bar{1}1)$ ,  $r(10\bar{1}2)$ ,  $y(20\bar{1}1)$ ,  $s(11\bar{2}1)$ ,  $v(11\bar{2}2)$ ,  $h(21\bar{3}0)$ ,  $e(21\bar{3}2)$ , and  $p(41\bar{5}2)$ ; hardness 4 to 5; no cleavage; colorless with glassy luster; sp. gr. 3.695. Compon:  $As_2O_3$  50.60,  $Sb_2O_3$  0.55,  $P_2O_5$  2.72,  $Al_2O_3$  0.34,  $CaO$  42.68,  $MgO$  0.56,  $Na_2O$  1.24,  $K_2O$  0.37,  $Cl$  0.54,  $F$  trace, insol. 1.00,  $H_2O$  (loss on ignition) 2.28, sum 102.85%. Formula is  $(Cl, F, OH)Ca_2As_2Sb_2O_{10}$  with some of the As replaced by P and Sb and some of the Ca replaced by Mg and alkalis. The  $H_2O$  is higher than the formula demands. Excess over 100% is probably due to the relatively large exptl. errors with the small amt. (0.31 g.) of material used.

W. S.

*Sarkinite from Långban, a new mineral from this locality*. G. FLINKE. *Geol. För. Förh.* 46, 661-70 (1924).—Crystals are tabular on the first pinacoid;  $a(100)$ ,  $b(010)$ ,  $c(001)$ ,  $m(110)$ ,  $p(021)$ ,  $s(032)$ ,  $q(011)$ ,  $e(101)$ ,  $d(201)$ ,  $f(301)$ ,  $k(211)$ ,  $l(432)$ ,  $r(421)$  and  $h(821)$ ; hardness 4 to 5; cleavage variable; color flesh red, varying from pale and transparent to dark blood-red and opaque; luster glassy.  $n' = 1.8085$ ,  $n'' = 1.8065$ ,  $n''' = 1.7930$ . Sp. gr. 4.178 (by pycnometer) and 4.173 (by hydrostatic weighing). Analysis:  $As_2O_3$  42.55,  $MnO$  50.60,  $FeO$  0.15,  $CaO$  1.09,  $MgO$  0.29,  $Na_2O$  1.30,  $H_2O$  3.41,  $Al_2O_3$  0.10, insol. 0.14, sum 99.66%. It is easily sol. in dil. acids, and all the As is quinquevalent. The formula is probably  $As_2O_3 \cdot 4MnO \cdot H_2O$ , with part of the Mn replaced by other elements.

W. SEGERBLOM

Presence of the compound,  $K_2Mn_2(SO_4)_4$ , among the products of the present ac-

tivity of Vesuvius. F. ZAMBONINI AND G. CAROZZI *Gazz. chim. ital* 55, 414-6 (1925).—  
See C. A. 19, 1876. H. G.

Two new finds of scheelite. B. K. ALMSTROM *Geol. For. Forh* 47, 135-6 (1925).—  
An unusually heavy mass the size of an egg found in the Gustafsberg Mine was composed  
of a white to grayish green transparent mineral with veins of a darker material. Sp  
gr. = 6.066. Analysis showed it to be scheelite,  $\text{WO}_3$  79.95,  $\text{CaO}$  19.63, sum 99.58%.

Blasting in Gothenburg revealed scheelite with sp gr 6.055. W. SEGERBLOM  
Catalog of Stockholm Högskola collection of new or incompletely described minerals  
from Långban. G. FLINK. *Geol. For. Forh* 46, 704-9 (1924); cf. C. A. 18, 2306.—  
New minerals numbered 209 to 315 continue the list already announced. W. S.

A new method of preparing briquetted mineral grains for microscopic study. R.  
E. HEAD *Eng. Mining J. Press* 119, 889-90 (1925).—Ten g. of mineral grains are  
mixed with 3 g. of redmanol. The mixt. is placed in a mold standing on a hot-plate at  
104°, and 5 min. allowed for fusion and settling. It is then pressed with a plunger,  
finishing in a vise that exerts a pressure of about 1 ton, where it is left to cool and the  
briquet then removed. The redmanol is unaffected by acids or low heat, the section  
may be highly polished, and the mineral grains do not pull out during polishing.  
A. BUTTS

Manganese-bearing river pebbles. E. DITTLER. *Min. Petr. Mitt* 36, 164-9  
(1924).—"Shiny pebbles" from the bed of the Vistula have a thin (1-2 mm) black coat-  
ing of Fe and Mn hydroxides, the smooth surface having a metallic luster. Analysis  
of a sandstone pebble gave: insol. in HCl (quartz grains) 90.84,  $\text{Mn}_2\text{O}_3$  (and  $\text{MnO}_2$ )  
1.14,  $\text{Fe}_2\text{O}_3$  3.67,  $\text{H}_2\text{O}$  4.19%; micro sections show the presence of psilomelane and limo-  
nite as the cementing material of the sand grains. Pebbles of mangandolomite from the  
Enns in Upper Austria show a dull black skin 1-2 mm in thickness. Analyses of the  
inner and outer portions show that Mn hydroxide has accumulated on the exterior at  
the expense of Mn carbonate. Expts. were made on the adsorption of Mn from a soln.  
of Mn H carbonate by quartz sand and other materials. Quartz sand took up 51.74%  
of the Mn from the soln., kaolin 68.73, compact limestone 72.90, marl 78.53, and pptd.  
chalk 96.53% (in the last case there being probably also chem. replacement). It is  
suggested that in the case of the "shiny pebbles" the Mn was taken up from the river  
water. B. C. A.

Inorganic origin of petroleum. E. PYHÄLÄ. *Petroleum Z.* 21, 975 (1925).—A his-  
torical review of theories concerning volcanoes, as applied to the theory of petroleum  
origin. D. F. BROWN

Seaweed fat and its significance for the question of the origin of petroleum. J.  
MARCUSSEN. *Chem.-Zig.* 49, 455-6 (1925).—Algae mud after drying and pulverizing  
was extd. first with ether and then with chloroform. 6.8% of extract was obtained  
having an acid number of 135, saponification no. 190, 1 no. 91, and contg. 12.4% un-  
saponifiable matter (higher alcohols). This is therefore a strongly hydrolyzed glyceride  
fat. Waxes have been extd. from algae from Ludwigholmen sea. During the decay of  
the algae a strong reducing effect is noticeable which appears to transform the unsatd.  
fatty acids and higher alcohols of the algae fat into waxes, which are more stable compds.  
than the fats. These waxes can later be transformed into petroleum. D. F. BROWN

The Taufkirchen region in Upper Austrian Innkreis and the occurrence of petroleum  
there. W. PETRASCHKE. *Petroleum Z.* 21, 1129-34 (1925).—The stratigraphy and  
tectonics of the region are described. The oil has a sp. gr. of 0.917 at 74.4° R., flash  
150°, cold test 7°, viscosity at 100° of 10° E., and an asphalt content of 1.5%. Distn.  
gives 79.6% distillate of 0.932 sp. gr. and cold test 10°; 14.4% asphalt coke and 7.93%  
loss. The origin of the oil is discussed. D. F. BROWN

Physical chemistry and igneous rock formation. ALEXANDER SCOTT. *Trans.*  
*Faraday Soc.* 20, 494-9 (1925).—S. discusses the factors, operating in natural magmas,  
which have not yet been duplicated in laboratory expts. The presence of water vapor  
in rocks is an especially important difference. E. F. H.

Eulysite from Västerbotten. A. HÖGBOM. *Geol. For. Forh* 46, 710-2 (1924).—  
In a mine, opened in 1838 at Bygdalsjåm but later abandoned, H. found in 1924 a eulysite  
rock contg. 4.5%  $\text{MnO}$ . This was accompanied by olivine, garnet, hedenbergite,  
autophyllite, graphite and magnetite. The rock is being further investigated, par-  
ticularly with reference to its genesis. W. SEGERBLOM

Sulfate deposits in lava tubes. R. H. FINCH AND O. H. EMERSON. *Am. J. Sci.*  
10, 39-40 (1925).—Sulfate deposits occur in recently formed lava tubes, near Kilauea.  
They are probably due to the leaching of wall rock in which silicates had been altered  
to sulfates by the action of steam-bearing  $\text{SO}_2$  and  $\text{SO}_3$  accompanying the passage of  
lava through the tubes. E. F. H.

Radioactive methods for the age determination of minerals. G. KIRSCH *Mitt. Petr. Mitt.* 36, 147-56(1921).—The trustworthiness of the method of detg. the age of minerals from the Pb (Ra-G)/U ratio is discussed. It is necessary to know the at. wt. of the Pb present in order to distinguish between primary Pb and Ra-G; and further, it is found that in specimens for which this has been detd., the compn. varies from piece to piece. New ests., in millions of years, are: for bröggerite from Moss, Norway, 805; pitchblende from Jáchymov, Bohemia, 207; uraninite from Morogoro, East Africa, 605; pitchblende from Katanga, Belgian Congo, 550. From the published data for thoranite from Ceylon, the half life-period for Th is calcd. as  $T = (1.65 \pm 0.03) \times 10^9$  years, and the age of the thoranite estd. at about 150 million years. The genetic relationship between U and Th is discussed, and for Th U is calcd.  $T = 63.2 \times 10^1$  or  $62.6 \times 10^4$  years. B. C. A.

Catalog of Swedish geological, paleontological, petrographic, and mineralogical literature for 1923. F. F. ÅHLANDER. *Geol. For. Forh.* 46, 696-703(1924).—Continues with 129 titles the list described in C. A. 18, 2309. W. SEGERBLOM

MORÉAU, GEORGE. Étude industrielle des gîtes métallifères. 2nd Ed., revised and enlarged. Paris: Ch. Béranger, 564 pp. Fr. 75.

VERNADSKII, V. La géochimie. Paris: Félix Alcan. 404 pp.

Luminescence in the Ingleside calcites affected by acids (HEADEN) 3. X-ray examination of inner structure of various Ca carbonates (OSAWA) 2.

## 9—METALLURGY AND METALLOGRAPHY.

D. J. DEMOREST, R. S. WILLIAMS

An outline of mining and metallurgical practice in Australasia. *Bull. Inst. Mining Met.* No. 250, 204 pp (1925). E. H.

Vanadium in iron ores and its extraction. RUGGER VON SEHN. *Eng. Mining J. Press* 120, 51-6(1925).—V, on smelting, practically all enters the pig iron, from which it is easily slagged and coned. A summary of investigations on ores contg. V and an account of its behavior in the furnace processes are given. A new method of extrn. is described in which V will be coned. about 50 times and obtained as a slag high in V, which can be worked as natural V ores. The Thomas-process pig iron is refined in acid converter. Si and Ti, most of the Mn and some C, but little or no P will be slagged with the V. The metal is put in a basic converter and is refined in the usual way. The only additional cost is for the converter and the labor connected with it. W. H. B.

The treatment of manganese-silver ores. G. H. CLEVENNER AND M. H. CARON. *Bur. Mines, Bull.* 226, 1-101(1925).—There is a refractory compd. of Mn and Ag which is insol. in cyanide soln. and other solvents for Ag. An oxidized ore contg. a refractory compd. of Ag and Mn upon being heated in a reducing atm. and cooled in a manner preventing reoxidation becomes amenable to cyanidation. Ores contg. Sb are notable exceptions. Details of app. and methods of making small-scale and working-scale tests are given. Numerous tables and a complete bibliography of the treatment are included. W. H. BOYNTON

Status of sand tests. I. H. RIES. *Foundry* 53, 531-4(1925).—The usual tests applied to sand are discussed and the importance of standardization of tests pointed out. Sieve tests are more rapid than elutriation tests. After sepn. into groups of grain size the best manner of expressing the results is important. Four plotting methods are shown. W. H. BOYNTON

Material and heat balance of a southern foundry furnace. S. P. KINNEY. *Blast Furnace & Steel Plant* 13, 272-7(1925).—The material and heat balance of a foundry furnace of the Central Iron and Coal Co. at Holt, Ala. are worked out. The material balance is shown in 5 tables and the heat balance is worked therefrom. Operating data are compared with those of 4 northern furnaces. The distribution of heat is shown. Certain const. quantities of heat are required for the reduction of iron oxide to metal, nearly const. for all furnaces. The southern furnace requires more heat over and above that to reduce the oxide. This increases as the Fe content of the ore decreases. W. H. BOYNTON

Magnesium as brass deoxidizer. C. V. NASS. *Foundry* 53, 527(1925).—Mg-Cu is unsatisfactory as a deoxidizer because a deleterious constituent is formed and some oxide is left in the metal. W. H. BOYNTON

The story of the production and uses of ductile tantalum. C. W. BALKE. *Smithsonian Rept. for 1923*, 233-9(1925).—B. discusses the occurrence of Ta, production of the metal, its phys and chem properties and uses. Its high chem resistivity, and its tendency to absorb gases are characteristic. It has possibilities as a cathode.

W. H. BOYNTON

Making cast stainless steel. J. M. QUINN. *Foundry* 53, 515-8, 525(1925).—Comparative exptl results are shown of 13%-Cr and 19%-Cr stainless steels. Heat treatments, slag control and costs are considered.

W. H. BOYNTON

Relation of metallography to physical research. J. CZOCHRALESKI. *Naturwissenschaften* 13, 425-35, 455-64, *Z. Metallkunde* 17, 1-11(1925).—For investigation of the details of structural change involved in deformation of metals the metallographic methods (etching of sections) are often better suited than X-ray investigation. This is demonstrated in a series of pictures of the plastic deformations (twisting, rolling) of single crystal Al rods. On the basis of these observations and of X-ray evidence (asterism of the interference points) it appears that the single crystals remain wholly intact during the deformations, contrary to Polanyi's translation hypothesis. In an extensive discussion of the anisotropic properties of metal crystals these phenomena are further explained.

B. J. C. VAN DER HOEVEN

Malleability and metallography of nickel. P. D. MERICA AND R. G. WALTEBERG. *Bur. of Standards, Tech. Paper* 19, 155-82(1925), *Trans. Am. Inst. Mining Met. Eng.* Feb. 1925, (advance copy) 8 pp.—Fleissmann in 1879 proposed the addition of Mg to Ni to promote soundness and malleability. This method is still used, and the authors have investigated the reasons for its success. Exptl crucible melts of Ni with additions of  $\text{Ni}_3\text{S}_2$ , Mn, Mg, etc. were made, tested for malleability, and studied with the microscope. NiO forms a eutectic, contg 0.24% O, with Ni, and alloys up to at least that O content are malleable. Ni is not rendered non-malleable by the presence of CO,  $\text{CO}_2$ ,  $\text{O}_2$ , or  $\text{N}_2$ . Small quantities of S make Ni non-malleable both hot and cold. S forms a eutectic with Ni melting at  $644^\circ$ , and occurring in the form of films around the Ni grains when over 0.005% S is present. S affects Monel metal in a similar way,  $\text{Cu}_2\text{S}$  being found when 0.01% S or more is present. C, Si, and As in small amts do not affect the malleability. Mn helps to overcome the bad effect of S, but Mg is more effective. Each will take the S from the Ni and by forming Mn or Mg sulfide eliminate the dangerous Ni sulfide. Thermal analyses, sulfur prints, and photomicrographs illustrate this action. MnS forms a eutectic with Ni, melting at  $1325^\circ$ . It occurs along the grain boundaries, but in small globules, not films like  $\text{Ni}_3\text{S}_2$ .  $\text{MgS}$  is insol. in molten Ni, and solid at  $1460^\circ$ . It occurs scattered through the Ni grains, is decomposed by water, and is pitted during ordinary polishing. Mg removes gases from molten Ni, and if oxidized its effect on S may be unpaired. An excess of Mg in Ni up to 0.5% does not affect the malleability, but in Monel metal 0.2% or more is harmful.

G. F. C.

The transformations in pure iron. KOTARO HONDA. *Sci. Repts., Tohoku Imp. Univ.* 13, 363-71(1925).—The  $A_1$  transformation in Fe is not a change of phase. A transformation involves a discontinuous change of properties, and a change of phase is a function of time. The elec. resistance at any temp. near the  $A_1$  point does not change with time. X-ray analysis shows that below the  $A_1$  point there is no change of configuration. The  $A_2$  change corresponds to the increase of the rotational energy about the magnetic axis of Fe atoms, the magnetic and thermal changes being due to the same cause. The magnetization does not fall abruptly at  $A_2$  except in weak fields, where a thermal effect interferes. It changes discontinuously at the  $A_1$  and  $A_4$  points.  $\beta$ -Fe is not an independent phase;  $\delta$ -Fe is the same phase as  $\alpha$ -Fe.

G. F. C.

The plastic deformation of  $\alpha$ - and  $\gamma$ -iron. F. C. THOMPSON AND W. E. W. MULLINGTON. *J. Iron Steel Inst. (London)* 109, 67-73(1924).—A discussion based on the X-ray investigations of Westgren (*C. A.* 16, 2291). The cryst. structure or atomic packing of  $\alpha$  iron is such that the unit cube contains an atom at each corner and one at the center of each face, the 111 plane of the cube being that of closest packing. Plastic deformation is pictured as rearrangement in this plane from cubic to hexagonal symmetry. If such gliding or rearrangement takes place in 2 intersecting 111 faces their intersection has the opposite symmetry from the faces proper and becomes a bar of twinned orientation, i. e., forms a Neumann lamella. In  $\gamma$ -iron the packing is such that the unit cube has an atom at each corner and one at its center, the plane of closest packing being the dodecahedral face 110. In this case the possibilities of rearrangement are greater, and may change the net closeness of packing, or d. It is shown that the movements and rearrangements that would logically be expected to take place under stress or fatigue conditions would produce d changes such as are actually observed.

Normally rearrangement would take place on the 100 or cube face, it being possible that cases of unexpected and unexplained brittleness are due to rearrangement of the 110 face due to some condition preventing movement on the 100 face. Wm. B. PLUMMER

Some physical properties of low-carbon steels. R. H. SMITH. *Trans. Am. Soc. Steel Treating* 7, 86b-80(1925); cf. C. A. 19, 1396.—A tabulation and description of practical heat treatment of low-C steel with accurate control of temp. and quenching. Phys. properties usually produced by quenching and drawing may be obtained in a single quench by accurately controlling the cooling medium, its velocity and temp., and the correct temp. of the steel from which the quench is made. A quenching device for com. production of rivets and bolts is described. W. A. MUDGE

The chemistry of iron and steel. F. T. SISCO. *Trans. Am. Soc. Steel Treating* 7, 197-214, 363-78, 491-517, 640-69(1925).—A series of articles selected primarily for their educational and informational character as distinguished from reports of investigations and research. W. A. MUDGE

The effect of repeated quenching on the hardness of carbon steels. ARATA KAYTO. *Sci. Repts., Tohoku Imp. Univ.* 13, 373-83(1925).—The hardness of 0.83% C steel after repeated quenches was measured with the scleroscope, and magnetically by the coercive force at a field intensity of 450 C. G. S. units. The hardness-quenching-temp. curves for mech. and magnetic hardness are similar, and nearly coincide above 760°. A forged specimen, quenched repeatedly at 750°, showed max. hardness at the second quenching. Preliminary heating at 600° did not improve the results from the first quenching. Magnetic tests showed that in the forged specimen the cementite was partially decomposed. The effective C content therefore was low, and a higher temp. was required for hardening until by the first heat-treatment the normal amt. of cementite was formed again. Other quenching expts. also indicated that imperfect hardening in oil may be due to the C remaining insol. at a comparatively low quenching temp. G. F. C.

Aluminum foundry alloys. A. L. ARCHBUTT. *Metal Ind.* (London) 26, 604-6, 626-8(1925); cf. C. A. 19, 1683-4.—An abstract. A comparison of the nature and properties of principal Al alloys used for castings. The mechanism of and constituents producing age-hardening are discussed. W. H. BOYNTON

Determination of the structural composition of alloys by a metallographical planimeter. E. P. POLUSHKIN. *Trans. Am. Inst. Min. Met. Eng.*, Dec. 1924, 19 pp.—The structural compn. of an alloy of 2 or 3 constituents may be detd. by planimetric measurement of the area occupied by each of the constituents on a few representative photomicrographs. This is accomplished by drawing a series of parallel lines at equal distances apart across the surface of the photograph so as to divide the constituents into a no. of trapezoids, the total area of which is found by multiplying the distance between 2 succeeding lines by the sum of the medians of the trapezoids as measured by a recording planimeter. The vol. occupied by a constituent of the alloy is then the same fraction of the total vol. of the alloy as the area of the constituent is to the whole area of the photograph. If the d. of each constituent is known, the weight of each present can be calcd. and thus the compn. of the alloy found. The application of the method to the analysis of some Bi alloys and of cast Fe is described; the results obtained agree reasonably closely with those found by chem. analysis. B. C. A.

A new aluminum alloy. V. FUSS. *Z. Metallkunde* 16, 343(1924); *Science Abstracts* 28A, 81-2.—The new alloy "Lautal" contains Cu and Si, with not more than 93% of Al, and the amt. of Fe usually found in com. Al. The treatment of the alloy is a combination of mech. and heat processes. Tensile strength 38 to 43 kg. per sq. mm. with an elongation of 18 to 23%; this can be raised to 60 kg. per sq. mm. by suitable mech. treatment, the elongation being lowered to 4%. The elastic limit of the normal alloy (see above) is 30 to 33 kg. per sq. mm.; cond. roughly 22 to 25 m./ohms sq. mm.; Young's modulus 600,000 to 700,000; normal hardness about 92 Brinell units increased by working; sp. gr. 2.7 to 2.8. The alloy resists the action of sea water and other corrosive agents, and is strong at high temps. Lautal can be worked with cutting tools, hammered out and drawn. The structure is not altered by age, so that the alloy does not become harder. H. G.

The oxidation of metals and alloys at high temperatures. YUKIYASU UYEDA AND MAKOTO SAITO. *Sci. Repts., Tohoku Imp. Univ.* 13, 391-9(1925).—The increase in wt. of Fe, Ni, Cu, Al, steel and nichrome wires due to oxidation at high temp. was measured with the thermobalance described by Endo (C. A. 19, 2622), continuously for 2 hrs. at each temp. The oxidation of Fe above 700° is rapid at first, but after an hr. the rate decreases. In piano-wire the oxide layer is less protective against further oxidation. The degree of oxidation of Ni is  $\frac{1}{10}$  that of Fe and steel. The oxide film

formed on Al at 500° and 600° prevents further oxidation. The oxidation of most elec. heater wires, such as nichrome, is relatively rapid for the first half hr., but afterward the compact oxide layers protect them. Chromel C, however, had a brittle oxide, and oxidized more. The resistance to oxidation varies inversely with the Fe content. G. F. C.

Endurance properties of alloys of nickel and of copper. III. D. J. MCADAM, JR. *Trans. Am. Soc. Steel Treating* 7, 581-617(1925); cf C. A. 19, 1845-6.—A study of the effect of cold working up to a 60% increase in tensile strength, on the rotating cantilever endurance properties of Ni. A few results of the effect of cold working on alternating-torsion endurance properties are given. The endurance limit of the 60% cold worked, annealed material is higher than that of the cold-worked material. Moderate cold working, a 15% increase in tensile strength, does not lower the endurance ratio of Ni or Monel metal. Cold-worked constantan, with a 47% increase in tensile strength, gave practically the same endurance ratio as the fully annealed alloy. W. A. M.

Hardness of copper-tin alloys. O. BAUER AND O. VOLLENBRUCK. *Z. Metallkunde* 16, 426-9(1924).—The curve showing the hardness of Cu-Sn alloys rises slowly with increase of Sn to 13.9%, the limit of the solid soln., then rapidly to a max. at the point corresponding with Cu<sub>3</sub>Sn; it then falls rapidly to a point corresponding with Cu<sub>5</sub>Sn<sub>6</sub>, after which the slope is gradual to pure Sn. A slight kink occurs in the downward portion of the curve at Cu<sub>3</sub>Sn. B. C. A.

Radio technic in the service of metallography. J. CZOCHRALESKI. *Z. anorg. allgem. Chem.* 144, 263-6(1925).—An Al-Si alloy is used as a detector in a radio circuit. A sample of alloy is connected in the circuit and placed under a microscope, and a needle connected to the earth through a pair of ear-phones is brought into contact with different parts of the surface of the alloy. That the alloy is not homogeneous is evidenced by the fact that there are areas where the detector action is very poor. C. believes that pure Si has sepd. from the melt and that the areas of poor detector action are due to these crystals of pure Si. The cause of the poor detector action of these crystals may be: (1) A new modification of Si is present; (2) the Si is very pure, because of recrystallization, and has lost its detector power as a result of loss of its impurities. R. J. H.

The chemical composition of rust. ROBERT STUMPER. *Bull. soc. chim. Belg.* 34, 150-8; *Chimie et industrie* 13, 906-10(1925), cf C. A. 18, 3353.—Analyses are given for 23 samples of rust, the limits of variation of the mol. compn. being 1-3 FeO.4-20 Fe<sub>2</sub>O<sub>3</sub>.2-22H<sub>2</sub>O. A series of expts. was made by suspending small steel plates in tap water and analyzing the total rust after varying lengths of time. The total FeO (mg. FeO from the total rust on a given plate) remained approx. const. after the 1st day, while the total Fe<sub>2</sub>O<sub>3</sub> increased uniformly. The % FeO (based on FeO plus Fe<sub>2</sub>O<sub>3</sub>) hence decreased from 45.3% at the 1st day to 9.5% on the 15th, the curve being approx. hyperbolic. This shows that after the initial period, the FeO is converted into Fe<sub>2</sub>O<sub>3</sub> by the air at the same rate that it is formed. WM. B. PLUMMER.

Protection of oil- and gas-field equipment against corrosion. R. VAN A. MILLS. U. S. Bur. Mines, *Bull.* 233, 120 pp.(1925).—The underground corrosion is electrochem.; it is most serious in saline acid waters. H<sub>2</sub>S corrodes ferrous materials even in alk. waters and seems to react directly with the iron. Corrosion products are sol. in water, increasing the cond. so that corrosion is self accentuating. Failure occurs by pitting and is explained by galvanic action. Analysis of waters from many fields are given. Cases of corrosion are described in detail with photographs. Prevention by mud-laden fluid or oil mud about the casing and by zinc castings in the well are the most promising methods until resistant alloys become commercially practical. E. L. CHAPPELL.

The corrosion problem in connection with water-works engineering. F. N. SPEGLER. *J. New Eng. Water Works Assoc.* 39, 90-100(1925).—The electrochem. theory of corrosion is described. With the exception of chem. corrosion and electrolysis by imposed currents the extent and rate of such corrosion is detd. by the dissolved-O content of the water. Alkalies usually decrease corrosion after a short time. This is mostly due to a formation of a protective coating by pptn of CaCO<sub>3</sub>. Na<sub>2</sub>SiO<sub>3</sub> produces a similar effect. Under water, wrought iron and steel are about equally resistant. Deaeration is advantageous in decreasing corrosion. R. E. G.

Action of natural waters on metallic copper. HERBERT HENSTOCK. *J. Soc. Chem. Ind.* 44, 219T(1925).—Natural water contg. NaCl or MgCl<sub>2</sub> attacks Cu pipes, etc. Distd. water boiled with copper for 100 hrs. gave no Cu test with ferrocyanide. This water with 0.003 parts per 100,000 of NaCl, KCl or MgCl<sub>2</sub> showed a Cu test in 2 hrs. while no test was shown after 48 hrs. boiling with similar concns. of CaCl<sub>2</sub>, MgSO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, etc. Water contg. org. matter showed no action. E. L. CHAPPELL.

Tests for grading corrosion-resisting alloys. WAR. E. ERICKSON AND A. L. KIRST.

*Metal Ind* (London) 26, 509-10(1925) —A simple means of obtaining a guide to the corrosion-resisting properties of metals and alloys is described. The principle and the method of the test are outlined and results of the deposition of the metal in soln. upon pure metals, and numerous ferrous and non-ferrous alloys are tabulated. The solns., successively more corrosive, used were:  $\text{CuSO}_4$ ,  $\text{AgNO}_3$ ,  $\text{PtCl}_4$ ,  $\text{AuCl}_3$  and  $\text{PdCl}_2$ . Generally speaking, Cr and Si are most resistant to corrosion. It is indicated that when these metals are present in quantity sufficient to prevent corrosion to a marked degree a solid soln. is formed by the two metals. The tests furnish a means of selecting from a large no. of alloys those that are highly resistant to corrosion and sepp. them into groups according to their probable resistance to it. Where atm. corrosion must be considered, this test should be supplemented by the acid test. W. H. BOYNTON.

Effect of grain size on the electromagnetic losses in dynamo and transformer sheets. K. DAEVES. *Stahl u. Eisen* 44, 1283-6(1924) —Sheets from the same heat of the same gage but rolled to different size sheets, have different hysteresis losses  $W_h$  and the losses have a nearly const. ratio to each other after different treatments. Annealing reduces  $1/2$  the grain elongation due to rolling but the relative grain-shape and hysteresis losses remain as before. Again, the edge portion of a sheet shows a different  $W_h$  from that of the middle, on account of differences in grain size incident to variations in temp. during rolling and therefore in the quantity of cold work received. The losses seem proportional to the number of grain boundaries traversed rather than to the grain size. The shape is therefore a factor. D.'s results on the effect of carbon, manganese, silicon and phosphorus content agree with those of Jensen (*J. Am. Elec. Eng.* May, 1924). A. H.

Resolving power, magnification and enlargement. W. M. MITCHELL. *Trans. Am. Soc. Steel Treating* 7, 618-34(1925). —The max. theoretical resolving power of the microscope is calculated for visual observations and for photomicrography, for both dry and immersion objective systems. From these are detd. the magnification necessary to show full detail resolved by the objective when used visually or photographically. The size of the silver grain in the emulsion det. the resolving power of the photographic plate. Enlargement, to obtain large photographs at high magnification, from small negatives is explained in terms of the advantages offered by the method. W. A. M.

Specific effect of alkalies in carburizing compounds. HUGH ROPMAN. *Trans. Am. Soc. Steel Treating* 7, 635-9(1925) —Lab. tests indicate that the energizing effect of carbonate additions varies with the position of the alkalies or alkaline earths in the periodic system. The energizing effect also increases with the increase of atomic wt. of the alkaline earth and decreases with the decrease of the atomic wt. of the alkalies.

W. A. MUDON.

Some notes on the twist test. C. BLAZEY. *Metal Industry* (London) 26, 529-31(1925) —Diagrams are given to show that in twisting Cu wire the number of grains appearing on a cross section does not change, while on a lengthwise medial section the no. of grains increases at the surface of the wire. In twisting to destruction, the surface grains may elongate over 700%, and appear several times on a single lengthwise section. The hardness of twisted wire is greater near the surface than at the core. The banded structure of arsenical Cu causes curved or looped etch patterns on longitudinal sections of twisted wire. These patterns are illustrated by photomicrographs. G. F. C.

The dynamic hardness of bronze, aluminium bronze and brass at high temperatures. TSUTOMU MATSUDA. *Sci. Repts., Tohoku Imp. Univ.* 13, 401-11(1925). —To supply the necessary data for the hot-working of Cu-Sn, Cu-Al and Cu-Zn alloys, and to confirm the effect of transformations, dynamic hardness tests were made at temps. up to 900° by dropping a hammer, carrying a 10 mm. steel ball, on the heated specimen and measuring the impression. The Cu-Sn specimens were cold rolled and annealed. The hardness of the  $\alpha$ -alloys decreased gradually with rise of temp., but in alloys of higher Sn content, there was a rapid decrease in hardness above the eutectoid point, on account of the softness of  $\beta$ . The Cu-Al specimens were rolled, drawn and annealed. The relation of hardness to temp. and compn. was the same as in the Cu-Sn alloys, the  $\beta$  existing above 570° being softer than  $\alpha$  plus  $\gamma$ . The brass specimens were treated in the same way, and the hardness of the  $\alpha$ -alloys decreased gradually with rise of temp. With less than 60% Cu, or with considerable  $\beta$ , in the brass, the hardness increased at low temp., reaching a max. at 300° to 400°, and decreasing above that. At lower temps. the hardness is generally greater with higher Zn content, but at higher temps. the reverse is generally true.

G. F. C.

The hardness of brass, aluminium bronze and bronze. T. MATSUDA AND J. SHIBA. *Sci. Repts., Tohoku Imp. Univ.* 13, 413-7(1925) —Hardness tests of brass (up to 50% Zn), Al bronze (up to 11% Al), and bronze (up to 21% Sn) were made by the Brinell, scleroscope, Martens scratch, and Matsuda dynamic methods, and are reported in

tables and curves. In the  $\alpha$ -range the hardness by all methods rises first rapidly and then slowly with decrease of Cu, but with increase of  $\beta$ - or eutectoid it rises more rapidly. The relations between the various scales of hardness were found rather complicated, and are discussed briefly. G. F. C.

Repeated-impact test on brass, aluminium bronze and bronze. TSUTOMU MATSUDA. *Sci. Repts., Tohoku Imp Univ* 13, 419-26(1925)—Stanton repeated-impact tests on rolled, drawn and annealed brasses gave a first max at 20 to 30% Zn. Increase of  $\beta$  in the brass gave much better results, but the presence of a trace of  $\gamma$  caused a very sudden drop. With annealed Al bronze, the Stanton results were raised up to 8% Al, but decreased with higher Al. When quenched, however, the Stanton no. of a 10% Al bronze was 5 or 6 times as high as when annealed. Similar results were obtained with annealed Cu-Sn alloys, the values decreasing above 13% Sn unless the bronze was quenched to suppress the formation of eutectoid. A brass of 67.5% Cu, annealed at different temps. up to 910°, showed increasing Stanton nos. up to 315°, then decreasing to 410°, with a lower max at 810°, followed by a sudden fall. The hardness showed a max at about 250°, followed by a steady fall. G. F. C.

The magnitude and distribution of internal strains in cold-worked brass. GEORG MASING AND CARL HAASE. *Wiss Veroeff Siemens* 4, 69-73(1925)—Rods of 70% Cu brass, 20 mm. diam and 200 mm long were annealed at 700° for 2 hrs. The surface was removed so as to expose the virgin metal and the rods were rolled to 20, 40 and 60% reduction. Strain measurements were made after 2 months. Tests were carried out according to Heyn and Bauer (*C A S*, 3037). The max strain is at the surface of the rods; this is directly opposed to results on drawn rods, where the max strain was found at or near the axis of the rods. C. G. F.

Typical static and fatigue tests on steel at elevated temperatures. T. McL. JASPER. *Proc. Am Soc Testing Materials* (preprint) June, 1925, 6 pp.—This paper gives the result of tensile-strength tests at various temps (up to 700°). Normalized steel shows an increase in tensile strength in the neighborhood of the blueing heat (around 300°) and a rapid falling off at higher temps. The same steel quenched and drawn at 190° has a much higher tensile strength at 20° but the value slowly decreases at higher temps to the same values obtained for the normalized product. There is, therefore, no advantage in heat treating when the material is to be used at or above the blueing temp. Long-time tensile-strength tests (12-72 hrs) were made by increasing the load gradually after the proportional limit was reached rapidly. The curves then obtained showed a much greater drop than those from ordinary static tests. The steel at higher temps. loses certain of its elastic properties and approaches the state of a plastic amorphous material. Alloy steels, especially those high in W, Ni and Cr, withstand stress at high temps. much better than straight steels. H. S. VAN KLOOSTER.

Some fatigue tests on non-ferrous metals. R. R. MOORE. *Proc. Am. Soc. Testing Materials* (preprint) June, 1925, 18 pp.—By means of an improved type of rotating-beam fatigue machine endurance tests were made on pure Mg, Al, naval brass and on forged and cast Mg-Al alloy (Al contents 8.68%). The ratio of endurance limit to sp. gr. shows that some light Mg alloys are more efficient than cold rolled plain carbon or alloy steel but not as efficient as some heat-treated alloy steels. An exact knowledge of the endurance limit is of far greater value to designers than the tensile strength, since in practice the material used never fails under a single application of an increasing load as is the case in a testing machine. H. S. VAN KLOOSTER.

Effect of thermal and mechanical treatments on the rate of solution of aluminium in hydrochloric acid. XAVIER WACHÉ AND GEORGES CHAUDRON. *Compt. rend.* 180, 1495-7(1925).—The effect of the Fe and Si contents on rate of soln. depends less on the % than on the distribution of these elements. The solid solns which they form with Al are less homogeneous the quicker the metal is cooled, and under these conditions the rate of soln. increases. Annealing and hammer hardening, which cause a uniform distribution of the Fe and Si, should decrease the rate of soln., this W. and C. prove explicitly. A. PAPIEAU-COUTURE.

Thickness of zinc coating in the hot-dip galvanizing process. HEINZ BABLIK. *Stahl u. Eisen* 44, 1370-1(1924).—The time in the Zn-bath has greatest effect; less important is the temp of the spelter. Higher temps. cause greater absorption. Thus at 420°, 1594 g. was absorbed and at 450°, 1775 g. Higher temps give more fluid spelter but high oxidation losses. The thickness of the sheet has no effect if not over 2 mm. High iron content in the bath is harmful, increasing the absorption greatly. Al addition reduces absorption sharply. Also with Al baths time of immersion has less effect. 0.5% Al plus 1% Sn gave low absorption. The compn. of the sheet steel affected absorption much less than did the structure. Automatic machines, control of temp and

Al content should allow maintaining of 500-600 g. Zn per square meter of sheet.

A. HUNCELMANN

Importance of venting, with special references to defective castings. E. LONGEN. *Metal Ind.* (London) 26, 489-90, 511-4, 534-8, 540(1925).

B. J. C.

Factors which influence the properties of cast iron. BOYER. *La fonderie moderne* 19, 47-8(1925) - To indicate the properties of cast iron, a chemical analysis should include the elements themselves and their chief combinations, for the latter are quite as important as the compn. B. suggests Fe, C, Si, Mn, S, P, As, Cu, graphite, combined C  $Fe_3C$ , and  $MnSi$ , should all be detd to give a proper index to the properties of cast iron.

C. G. KING

Results obtained in the study of the expansion of cast iron. PIERRE CHEVENARD AND ALBERT PORTEVIN. *Compt. rend.* 180, 1492-5(1925); cf. C. A. 11, 2743, 2765, 2881 - The study of the expansion of cast Fe by means of the differential dilatometer gives an insight into the complex transformations which occur during heating and cooling, and constitutes a better and more complete method of quant. and qual. analysis than the thermal method for phenomena occurring in solids, which is exemplified in the case of the effect of Si on graphitization of white cast Fe. The dilatometer shows that Mn and Cr cause a regression of the Curie point practically proportional to the Mn and Cr contents, showing that Mn and Cr carbides form a solid soln with  $Fe_3C$ , and the term "complex cementites" should be used instead of "double carbides." The globular form assumed by certain complex cementites in special steels is not characteristic but is due to the effect of the special elements on the coalescence of the cementite (P and Bernard, C. A. 16, 399). Variations in the concn. of cementite can be followed by means of the position of the Curie point, which allows of following variations in the partition coeff. of Mn between the carbide and ferrite according to annealing temp., the Curie point regressing with increase in annealing temp. A. PAPINEAU-COUTURE

Bronze-welding cast-iron pipe. R. F. STARKE. *Gas u. Wasserfachs.* 68, 349-55 (1925) - In strength tests on 12-m lengths of pipe contg. 2 welded joints, the pipe was placed on supports 11 m. apart and was loaded at its middle. Fracture in no case occurred at the weld, but usually was near it; for 15-cm pipe the max. deflection was 15 cm, the breaking load 390 kg; for 20-cm. pipe, 12 cm, 1200 kg; for 30 cm. pipe, 7 cm, 2950 kg. Hydraulic tests carried out after such a pipe had been loaded almost to fracture in no case showed leakage. Corrosion tests with 1% HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, or 10% NH<sub>4</sub>Cl or NaCl inside the pipe showed no serious attack; attack on the outside of the weld can be prevented by suitable protective coatings. Welding methods and costs are discussed.

WM. B. PLUMMER

The influence of metal temperature upon aluminium casting, and temperature measurement in molten aluminium. VON ZERLEDER. *Metall u. Erz* 22, 54-8(1925) -

C. G. KING

Tin solder and its manufacture. E. RICHARZ. *Chem.-Ztg.* 49, 360-70(1925). - An outline of the current method for making Sn solder from scrap metal and bearing-metal residues rich in Sn.

H. S. VAN KLOOSTER

Ternary system Cr-Ni-Mo (SIEDSCHLAG) 2. Ternary system Mo-Ni-Si (PFAUTSCH) 2. The inorganic dust of respiratory air in industrial trades and its gravimetric estimation (FRÖBOESE) 13. Deformation and recrystallization structures of metals (GLOCKER) 2. Furnace for heat-treatment of rods or bars of metal (U. S. pat. 1,543,714) 1. Crucible (for melting metals) (U. S. pat. 1,543,905) 1. Furnace for melting metals in crucibles (U. S. pat. 1,545,008) 1. Carbonizing coal, etc., and reducing ores (Brit. pat. 227,880) 21.

Extracting metals from ores. H. N. TRACY. U. S. 1,544,957, July 7. Ore contg. free metals is passed over the surface of a liquid metal, e. g., molten Pb, with which the ore is brought into intimate contact, in order to collect the metal values.

Recovering metals from silicate wastes. H. P. SOULIER-CORTINEAU. U. S. 1,544,493, June 30. Wastes such as those from metallurgical processes, from which metal values are to be recovered, in pulverized form, are mixed with a small proportion of fluor spar and treated with NaNO<sub>3</sub> and acid, e. g., H<sub>2</sub>SO<sub>4</sub>, to disintegrate the silicates. The metals liberated are oxidized and dissolved in the excess acid.

Reducing ores. H. G. FLODIN AND E. G. T. GUSTAFSSON. Brit. 227,435, Jan. 12, 1924. Fe ore and carbonaceous material in finely divided condition is mixed with a binder, the mixt. is dried and hardened and smelted in an elec. furnace. If the ore contains S, lime may be added to the charge and alloy Fe or steels may be produced by adding ores contg. Mn, Cr, V, etc. The metal first obtained may be further refined

in an open-hearth or elec. furnace or converter. A slag rich in P and suitable for use as a fertilizer may be obtained from ores high in P.

**Treating copper ores.** J. T. TERRY. U. S. 1,544,197, June 30.  $C_2H_2$  is introduced into a neutral or slightly acid soln. contg. Cu extd. from ore, in the presence of  $FeSO_4$  or other Fe salt to ppt. acetylide of Cu. This ppt. is sepd. without contact with air. Ores of Ag, Hg, Ni, Os and Pd may be similarly treated. Cf. C. A. 19, 2184.

**Treating zinc ores.** A. NATHANSOHN and F. LEYSER. Brit. 227,301, Feb. 18, 1924. Roasted Zn bearing ores or products such as spess, tutty or similar materials are leached with an acid soln. of an alk. earth chloride preferably contg. Cl 200 g. or more per l. at a temp. above  $60^\circ$ . Part of the Zn may be preliminarily extd. with dil. HCl or  $H_2SO_4$  in a counter-current process and the remaining Zn, Cu, Pb and Ag then extd. with the chloride soln. A final nearly pure  $BaSO_4$  residue is obtained from Rammelsberg ores.

**Treating lead-zinc ores.** A. NATHANSOHN. Brit. 227,660, Feb. 28, 1924. A roasted Pb-Zn ore is leached with a concd. soln. of  $MgCl_2$  or an alk. earth metal chloride preferably contg. over 200 g. of Cl per l. without addn. of acid, to dissolve Pb selectively. The residue is freed from Cl by  $H_2O$  and lime and treated for Zn recovery. Ag present may be dissolved with the Pb by adding Br. bleaching powder, peroxides, persulfates or permanganates and may be pptd. with Zn or Fe powder.

**Tin from oxide ore.** E. B. THORNHILL. U. S. 1,544,198, June 30. Oxide ore of Sn is heated in a reducing atm. together with carbonaceous material and without fluxing agents, to effect selective reduction and melting of the Sn without fluxing the gang or producing slag.

**Tin recovery.** F. WDSR. Brit. 228,103, Jan. 22, 1924. Metallic Sn and alloys contg. Fe and Si are obtained as sep. layers in recovering Sn from Fe-Sn alloys, by the addn. of Si or ferro-Si to the molten alloy.

**Copper from slag.** H. H. SPOUR. U. S. 1,544,048, June 30. A charge of molten Cu metallurgical slag is treated with metallic Fe and the mixt. is heated to effect fusion of the Fe and its distribution throughout the slag charge so that the Fe replaces the Cu in combined form and ppts. the Cu content of the slag.

**Reducing iron ores.** A. STANSFIELD. U. S. 1,544,111, June 30. A preheated mixt. of powd. Fe ore and carbonaceous material is introduced into the coolest end of a reducing chamber and the mixt. is passed with violent agitation in zones of increasing temp. against a counter-current of reducing gases.

**Chloridizing roasting of burnt pyrites.** J. SMON. U. S. 1,545,359, July 7. In chloridizing roasting of burnt pyrites or similar material, the charge is passed downwardly *en masse* through an air-tight stationary shaft, counter-current to an upwardly moving current of air.

**Apparatus for extracting precious metals with cyanide.** G. E. C. ROUSSEAU. Brit. 227,689, April 24, 1924.

**Iron and slag cement.** E. C. ECKEL. Brit. 227,837, Jan. 14, 1924. Ti-bearing Fe ore and limestone are heated to  $1400-1500^\circ$  to effect fusion, and Fe is tapped off from the bottom of the furnace. The upper layer of slag is withdrawn, cooled and ground to form a cement which may comprise Ca titanate and may contain in combination: lime 25-45, Si and Fe oxides together less than 20 and Ti oxide 10-60%.

**Cementation of iron, etc.** GELSENKIRCHENER BERGWERKS AKT.-GES. ABTEILUNG SCHALKE. Brit. 228,099, Jan. 24, 1924. In cementing ferrous metals with  $CH_4$ , the H formed is maintained below the limits at which the reaction ceases or reverses; e. g., in treating Fe under atm. pressure and at  $300^\circ$ , the H should not exceed 1.7%; at  $445^\circ$  3.4% and at  $508^\circ$  8%.

**Hardening steel articles.** D. S. O'DONOVAN. Brit. 228,096, Jan. 25, 1924. In hardening steel articles by processes such as covered by Brit. 205,037, the strength of the magnetic field is adjusted by varying the strength of the inducing current. Various mech. details are described.

**Welding steel and iron, etc.** K. ROSAK and SCHNELL-WERKEZEUG GES. Brit. 227,166, Oct. 5, 1923. In welding tool steel cutting edges on to tools with an Fe body or in welding similar metals one of which blisters when sufficiently heated, the surfaces to be joined are treated with Cu and borax or other deoxidizing medium stable at the welding temp. and are then heated together to over  $1200^\circ$  to effect blistering and union of the metals without use of pressure.

**Apparatus for heat-treating iron and steel articles with molten and surface-hardening substances.** F. M. CRAPO and W. BAYLIS. U. S. 1,545,305, July 7.

**Copper-coating iron or steel articles.** R. H. CHRIST. U. S. 1,545,127, July 7. Articles of Fe or steel contg. 1% or more Cu are heated to above  $690^\circ$  in an oxidizing

atm. and then cooled, to form a film-coating of Cu coated with Fe oxide scale. The scale may be removed with molten borax.

**Heat-treating and galvanizing iron.** OHIO BRASS CO. Brit. 227,873, July 15, 1923. Malleabilized cast Fe (e. g., an Fe contg. 2-10% C) is heated to a temp. in excess of that which will cause the Fe to be embrittled and quenched before the C-combining or crit temp is reached. It may then be treated with molten Zn or may be sherardized.

**Muffle furnace for heat-treating steel drills, etc.** D. S. O'DONOVAN. Brit. 228,098 Jan. 25, 1924.

**Apparatus for galvanizing iron or steel wire.** J. L. HERMAN. Brit. 228,082, July 21, 1923.

**Apparatus for galvanizing iron or steel wire.** J. L. HERMAN. Brit. 227,875, July 21, 1923.

**Aluminium alloys.** SOC. ANON. NIETPORT ASTRA. Brit. 228,143, Jan. 23, 1924. A light alloy comprises Al 93.3, Cu 3.4, Ni 1, Zn 1.8 and Mg 0.5%. This alloy is made by first prepg. an alloy of Cu 54.5, Ni 16.5 and Zn 29%, deoxidizing this with baryta, adding 100 kg. molten Al to each 6.5 kg. of the molten product, then adding 500 g. Mg and 2 kg. NaOH and casting at a temp. of about 700°.

**Silicon-zirconium alloys.** A. L. FERB. U. S. 1,544,824, July 7. Zr bearing material is reduced with carbonaceous material and there is used in the reducing charge such a quantity of Si that a low C alloy contg. more Si than Zr is produced. The Si content of this alloy is then reduced by the action of an alk. solvent for Si, e. g., a 20% NaOH soln.

**Copper-nickel-zinc alloy.** J. O. WILSON. U. S. 1,545,112, July 7. An alloy which may be used as a substitute for brass or Ni comprises Cu 1090-1150, Ni 2-0-320, Zn 475-530, B 4-10, Sn 18-22, Mn 20-35, Pb 55-65 and P 0.25-1.0 part.

**Steel alloy.** D. J. GILES. U. S. 1,545,094, July 7. An alloy adapted for making engine valves or valve seats or sleeves comprises Fe together with U or V 0.2-2.0, W or Mo 2-7, Co 0.2-5.0, Cr 2-8, Si 0.15-3.0 and C 0.2-1.5% and is free from any additional elements which would alter the resistance of the metal to wear or development of fire cracks when used under high-temp. service conditions. U. S. 1,545,095 specifies a similar alloy except that the U or V is omitted.

**Platinum alloy.** A. COHN. U. S. 1,545,234, July 7. Alloys which are adapted for manuf. of jewelry, etc. comprise Pt together with 1-15% of Ru.

**Cobalt, chromium and tungsten alloy.** B. M. HUFF. U. S. 1,543,921, June 30. An alloy which is suitable for making cutting tools contains Co 40-50, Cr 25-35, W 5-15, Mn 1-1.5, Fe 0-3 and Si 1-3%.

**Nickel-chromium alloy.** M. J. ROSENCRANTZ. U. S. 1,544,036, June 30. An alloy is prepd. by melting Ni and Cr and a previously formed alloy of Ni and Cr which has been treated with Zr while molten. Mo also may be added. U. S. 1,544,037 also specifies melting Ni and Cr together and adding Zr to the melt.

**Bronze.** H. H. SMITH. U. S. 1,544,108, June 30. A "foundation metal" is prepd. by fusing together Sn 40, Zn 10 and phosphor-Cu 1 part, approx. 500 parts Cu is separately heated to a temp. of about 1200° and the foundation metal and Cu are then fused together.

**Metal castings.** N. M. ARSTEN. U. S. 1,544,344, July 7. A material such as Mo, Cr, C, Co, Si, Mn, Cu, W, Ti or Al which will effect a change in the internal structure of the casting is caused to diffuse into the interior of a mass of molten metal, e. g., in casting rolls, in a mold.

**Iron castings.** P. A. DIEFENTHALE and K. SIPP. U. S. 1,544,502, July 7. In producing Fe castings of great strength and moderate Brinell hardness, a metal of low C and Si content is used which is cooled in molds preheated according to a temp. curve which with all mixts. having a const. C plus Si content rises in approx. a straight line as the wall thickness of the casting gradually increases.

**Casting aluminium or other metals.** C. PACE. U. S. 1,544,929, July 7. Castings with internal undercuts are formed about a core of brass or other acid-sol. material which is sepd. from the casting by dissolving in HNO<sub>3</sub> or other acid. U. S. 1,544,930 specifies casting Al-Cu alloy or other metal at a temp. above the m. p. of the core used (which may be formed of Al) but not contg. sufficient heat to melt the core.

**Castings with chromium-alloy surfaces.** W. M. MITCHELL. U. S. 1,545,438, July 7. Metals such as steel are cast in molds which are coated with Cr and a binder, e. g., Na silicate or "glutrin." The portion of the mold where washing during pouring would be excessive is coated with relatively fine Cr to prevent denudation during pouring of the molten metal into the mold.

**Casting magnesium.** O. WILHELMY. U. S. 1,544,710, July 7. A core is formed

from sand with a binder contg. waterglass, the latter is substantially dehydrated, and molten Mg is cast in a mold around the core.

Pickling sheet metal. J. B. TYTUS. U. S. 1,544,506, June 30. Mech. features. Furnace for annealing copper sheets, etc. F. L. ANTISILL. U. S. 1,544,702, July 7. Continuous kiln for annealing billets, etc. C. DRESSLER. U. S. 1,543,830, June 30.

Lining composition for iron molds. D. H. MCLOURE. Brit. 227,425, Jan. 12, 1924. A wash formed of lampblack 17, fireclay or other refractory substance 33, Na silicate 5, and  $H_2O$  45 parts or more is applied repeatedly to heated Fe molds for casting non-ferrous metals.

Welding aluminium. J. W. MEADOWCROFT. Brit. 227,471, Jan. 12, 1924. A flux for welding Al, duralumin or similar metals is prepd by grinding with  $H_2O$  a mixt. formed from  $KCl$  3.7,  $LiCl$  6.9,  $K_2CO_3$  3,  $Na_2CO_3$  38.2,  $K_2SO_4$  7.2, borax 20 and  $H_3BO_3$  21 parts. This flux is applied to a filler body of Al or similar metal and dried on it.

Welding rod. F. M. BECKET. U. S. 1,544,422, June 30. See Can. 245,594 (C. A. 19, 632).

Flux for soldering. M. LEVY. Brit. 227,903, Oct. 20, 1923. A mixt. of borax 8 and Na phosphate 2 parts is heated to 800–900° and the resulting glassy material may be used as a flux for hard soldering, e. g., by mixing the flux with 9 times as much powd. soldering metal and encasing the mixt. in a tube of hard soldering metal.

## 10—ORGANIC CHEMISTRY

CHAS. A. ROUILLER AND CLARENCE J. WEST

The future of the synthetic organic chemical industry in America. C. H. HERTY. *J. Chem. Education* 2, 519–32 (1925).

Theory of color production. JULIUS STIEGLITZ. *J. Franklin Inst.* 200, 35–49 (1925).—See C. A. 18, 1244.

Catalysis by the action of subdivided metals. III. Heat of adsorption of hydrogen on nickel. B. FORESTI. *Gazz. chim. ital.* 55, 185–201 (1925).—The work of Rideal (C. A. 16, 1389), of Gauger and Taylor (C. A. 17, 1913), of F. (C. A. 18, 1224), and of Beebe and Taylor (C. A. 18, 1228) is reviewed. B. and T. found that if their Ni was roasted 20 hrs. at 450° there is a diminution of about half in the adsorbing power for  $H_2$ , while there was a notable increase in the mol. heat of adsorption from about 15,500 to nearly 21,000 cal. According to this result the Ni having the greatest adsorbing power and thus most active as a catalyst also had the smaller heat of adsorption. F. considered that the temp. of evacuation used by him (0°) and by B. and T. (300°) might cause part of the difference in the results. A series of 36 detns. at temps. of evacuation from 300° to 0° was made: Temp. of evacuation 300° and 0°,  $H_2$  adsorbed 57.8 and 8.2, heat of adsorption 15,800 and 10,465 cal. resp. The intermediate values were of the expected order to conform with the extremes. When the Ni was previously roasted for 13 hrs. at 400–20° and evacuated at 300° the heat of adsorption was 15,230 cal.; roasting 65 hrs. at 450–70° and evacuation at 300° gave 14,500 cal. When all specimens were roasted 60 hrs. at 430–70° and 1 was evacuated at 300° the heat of adsorption was 14,800 cal.; if evacuated at 0° it was 10,175 cal. These results do not agree with those of B. and T. F. concludes that probably the surface of subdivided Ni (and other metals) is constituted of adsorbing centers of various power and that the catalytic activity depends on which centers capable of adsorbing the gas form the strongest bonds with it. F. discusses the manner in which the  $H_2$  is held at considerable length without arriving at a positive conclusion.

3,3-Diethylpentane (tetraethylmethane). G. T. MORGAN, S. R. CARTER AND A. R. DUCK. *J. Chem. Soc.* 127, 1252–9 (1925).—Triethylcarbinyl iodide,  $b_{112}$  71.2°,  $b_{127}$  153° (cor.),  $d_4^{20}$  1.42. With  $ZnEt_4$  this yields 3,3-diethylpentane,  $m$  –41 ± 1°,  $b_{112}$  139.2° (cor.),  $d_4$  0.75651, 0.75222, 0.74808, 0.74178 and 0.73758 at 15°, 20°, 25°, 30° and 40°; coeff. of cubical expansion, 15–30°, 0.001011; mol. vol., 15°, 169.4 cc.; co-volume, 16.3°; at. vol. of central C atom, 12.1; vapor d., 62.8; hence there is no association in the liquid state. Surface tension,  $\gamma$ , and mol. surface energy,  $\gamma V_m^{1/3}$ , 20°, 22.92, 704.5; 25°, 22.45, 692.2; 30°, 21.99, 680.4; 40°, 21.23, 661.1. Since the temp. coeff. is 2.17, 20–40°, the hydrocarbon is not associated in the liquid state.  $n_D^{20}$  1.42057,  $R_L$  43.06,  $r_D$  71.48 (calcd., 43.53, 71.79). Various comparisons are made of the phys. properties and chem. structure of allied paraffins and of homologs of the periodic group.

C. J. West

Inner oxidation reactions in addition compounds of nitrogen tetroxide and olefins. ALFRED SCHAARSCHMIDT AND HERMANN HOFMEIER. *Ber.* 58B, 1047-54 (1925); *C. A.* 19, 942 — From the different ways in which  $N_2O_4$  adds to olefins, S. had concluded that it exists in various forms in a definite equilibrium. These different forms manifest themselves only in the addn. to aliphatic olefins. The reaction with aromatic hydrocarbons activated with  $AlCl_3$  is much more nearly homogeneous; if the addn. is effected at low temps., an oxidizing action of the  $N_2O_4$  predominates over the purely nitrating action, and in the addn. to olefins low temps. also favor the oxidizing action of the  $N_2O_4$ . In the absence of  $AlCl_3$ , on the other hand,  $C_6H_6$  and  $PhMe$  react very slowly but, together with  $NO_2$  products, much nitrates or nitrates of phenols are formed. This also supports the view that there exist isomeric forms of  $N_2O_4$  which differ from each other in their chemical behavior and whose formation depends on the temp. The olefin addn. compds. undergo auto-decompn. even at room temps. (slowly, to be sure), with formation of large amts. of gaseous products. The present paper is a report of a study of the nature of these gases and of the influence on the decompn. of temp. and the presence of moisture during the addn. of the  $N_2O_4$  to the olefins used (cyclohexene (I), amylene (II) and cetene (III)). As the addn. is accompanied by a large evolution of heat S. and H. used as diluent benzene completely freed of unsatd. compds. and previously treated for some time with  $N_2O_4$ . The reaction products are in general insol. in this solvent and can therefore be easily sepd., but it has the disadvantage that more or less of its vapors are carried over with the gases and greatly interfere with the analysis of the latter. In 1 expt. in which  $CCl_4$  was used, on addn. of the 1st drop of the  $N_2O_4$  soln. at  $-16^\circ$  the temp. of the reaction mixt. rose, in spite of vigorous cooling, to  $30^\circ$ , and gas was evolved so stormily that the app. was shattered; apparently the  $CCl_4$  catalytically accelerated the reaction. With I, the evolution of gas, at first only very weak, becomes more vigorous as the soln. warms up spontaneously (generally to about  $30^\circ$ ); at  $60-70^\circ$ , a 2nd decompn., very slow at room temp., sets in, again with spontaneous evolution of heat and lively liberation of gas, and a 3rd, energetic auto-decompn. occurs when the yellow oily product is heated to  $140-50^\circ$ . The gas liberated during the addn. of the  $N_2O_4$  and the subsequent spontaneous rise in temp. consists chiefly of N; no  $N_2O$  could be detected. The gas evolved in the 2nd phase contains much N but also considerable  $NO$ . With II, gas is also energetically evolved twice: during the spontaneous heating to  $63-8^\circ$  and again on heating to about  $80^\circ$ . The 1st gas in this case already contains considerable  $NO$ , the 2nd gas about 30%. With III, the reaction is milder; the mixt. warms up spontaneously only to about  $30^\circ$  and evolves only an insignificant amt. of gas, a 2nd evolution occurring at  $90^\circ$ . The combined gases contained 87% N and about 10%  $NO$ . These facts show that during the addn. of the  $N_2O_4$  oxidation reactions set in, with the formation of considerable amts. of N. Furthermore, the addn. products also undergo inner oxidation reactions whereby the N oxide residues are in great part reduced clear down to N. Along with these reactions there occur reactions of the N oxides with the  $H_2O$  of oxidation, with formation of  $HNO_3$ , which in turn decomps. into  $HNO_2$  +  $NO$  and thereby likewise initiates oxidation processes. The instability of the addn. products is materially influenced by the temp. at which the  $N_2O_4$  is added. Care must be taken to dissipate the heat of addn. by cooling below  $0^\circ$ , otherwise the temp. may easily rise to such a point that the addn. product will decomp. violently. At still lower temps. ( $-30^\circ$  to  $-40^\circ$ ), there apparently occur chiefly complicated oxidation reactions with formation of exceedingly unstable oils. Thus in an expt. with I at  $-50^\circ$ , when, after the addn. was finished, the temp. rose to  $-20^\circ$  explosive decompn., with shattering of the app., occurred. Small amts. of  $H_2O$  ( $HNO_3$  and  $N_2O_5$ ) in the  $N_2O_4$  have a distinct influence on the reaction; after the addn. of traces of  $H_2O$  the addn. products of I have a higher reaction temp. than those obtained with dry  $N_2O_4$ .

C. A. R.

Adsorption and heterogeneous catalysis. I. L. V. ALEXEYEVSKII. *J. Russ. Phys.-Chem. Soc.* 55, 401-25 (1924) — A. Adsorption. A time-saving method of studying adsorption of vapors by solids was applied by passing over the adsorbers, placed in a tube, a current of air carrying the vapors under investigation. The magnitude of adsorption of  $H_2O$  vapors by carbo animalis purissimus (I) and the time of reaching equil. were detd. for ignited, not ignited, heated ( $110^\circ$ ) and regenerated charcoal, resp. By substituting the charcoal by calcined  $CuSO_4$  analogous expts. were made for comparison. By plotting the wt. of adsorbed vapors per unit wt. of adsorber against time, curves are obtained illustrating the velocity of adsorption until equil. is reached.  $C_6H_6$  and  $C_6H_5$  require 30 mins. EtOH, AcOH about 24 hrs. The magnitude of adsorption by 1 l. of vapors of 72 org. compds. and of  $Br_2$  are listed. The results do not permit of formulating a law, some rules being derived, however. Adsorption is highest

with  $\text{AmONO}$  (376%), second are aliphatic halogen compds. (up to 123.7%). Increasing mol. wt. of  $\text{C}_2\text{H}_5$  homologs and halogen derivs. of  $\text{C}_2\text{H}_5$  corresponds with increasing affinity; the reverse is shown by aliphatic ethers and aldehydes,  $\text{C}_2\text{H}_5$ , aromatic nitro compds. and amino derivs. of  $\text{C}_2\text{H}_5$ . Introduction of  $\text{HO}$  groups decreases the adsorption. In general adsorption is dependent on chem. forces, phys. const. mostly having no influence, e. g., especially evident with  $N$  heterocyclic compds. B. Catalytic action of animal charcoal.  $\text{C}_2\text{H}_4$  and  $\text{Cl}_2$  gave 80%  $\text{syn-C}_2\text{H}_4\text{Cl}_2$ , after having been passed over I at  $120^\circ$ . The action on  $\text{C}_2\text{H}_4$  mixed with other gases is being investigated.

H. BERNHARD

**Methylphenylbutadiene.** CHARLES PRÉVOST. *Compt. rend.* 180, 1851-3 (1925).—Addn. of  $\text{Ph}(\text{CHBr})\text{Me}$  in small portions to alc.  $\text{KOH}$  boiling at  $100^\circ$ , maintaining the soln. at this temp. for 0.5 hr. and extg. by the ordinary means, gives impure methylphenylbutadiene,  $b_p$  128.5°. Cooled in a current of  $\text{MeCl}$  it solidifies, and after fractional crystn. it m.  $22.3^\circ$ , with  $n_D^{21}$  1.6368,  $d_4^{21}$  0.9745, mol. refraction 51.53 (above the theoretical of 45.678 like  $\text{PhC}(\text{CPh})(\text{HC}(\text{C}(\text{C}(\text{H})_3)\text{CH}))$ ). Above  $22.3^\circ$  it is colorless, with low viscosity, has an aromatic odor and is very refractive and dispersive. It forms very large crystals, a small crystal on immersion absorbing several g. of liquid to form a larger crystal. The latter crystals are orthorhombic, comprising rectangular tablets with numerous facets. They are uniaxial with Na light, the axis being normal to the plane of the tablets, but biaxial with other radiation and they give magnificent figures between crossed nicol prisms with convergent light. Addn. of  $\text{Br}$  to a  $\text{CCl}_4$  soln. and evapn. gives the compd.  $\text{PhCBr}(\text{CBr}(\text{CBr}(\text{Me}))\text{CH})$ , m.  $97.7^\circ$ . On fractional crystn. of this in benzine and  $\text{HOAc}$  is obtained a bromide of the same % compn., which m.  $127-31^\circ$ , indicating that at least 2 of the 4 possible stereoisomers are present.

C. C. DAVIS

**Diacetylene.** LESPIEAU AND CHARLES PRÉVOST. *Bull. soc. chim.* 37, 704-11 (1925).—See C. A. 19, 1693.

E. H.

**Rapid preparation of cetyl alcohol.** M. A. YOUTZ. *J. Am. Chem. Soc.* 47, 2252-4 (1925).—A mixt. of 100 cc. 95%  $\text{EtOH}$  and 100 g. spermaceti is heated until the wax melts, 12 g.  $\text{KOH}$  in 10-12 cc.  $\text{H}_2\text{O}$  added slowly and the soln. warmed and agitated for 15 min. It is then transferred to a separatory funnel, the flask washed with 75 cc.  $\text{H}_2\text{O}$  and 200 cc.  $\text{H}_2\text{O}$  and while warm, 400 cc. petroleum ether is added and the mixt. shaken. The aq. layer is extd. 4-8 times with 200 cc. petroleum ether; yield 44.8%; calcd., 51.4%; m.  $45-6^\circ$ . The alc. is best purified through the acetate,  $b_p$   $184^\circ$ , m.  $22.7^\circ$ .

C. J. WEST

**Exchange of functional groups between two molecules.** Exchange of alcohol and aldehyde groups. A. VERLEY. *Bull. soc. chim.* 37, 537-42 (1925).—Dry  $\text{Al}(\text{OEt})_3$  causes the following condensation:  $2\text{RCHO} = \text{RCO}_2\text{CH}_2\text{R}$  (Titschenko).  $\text{Al}(\text{OEt})_3$  in the presence of excess alc. causes the following reaction:  $\text{RCHO} + \text{MeCH}_2\text{OH} = \text{RCH}_2\text{OH} + \text{MeCHO}$ . The T. reaction occurs only as a secondary reaction in this case. Thus, 300 g. citronellal gives 180 g. citronellol and 25 g. citronellie acid. This reaction, like that of T., is a general one.  $\text{PhCH}(\text{CH}_3)\text{CHO}$ , which cannot readily be reduced to cinnamic alc. by the usual methods, yields the alc. easily by this method. A result equiv. to an oxidation can also be obtained. Thus,  $\text{PrCHO}$  and  $\text{Al}$  geranylate in excess of geraniol give  $\text{BuOH}$ ,  $\text{PrCO}_2\text{Bu}$ , geraniol, geranyl butyrate,  $\text{Bu}$  geranate, and geranyl geranate. The results are identical if  $\text{Mg}(\text{OEt})_2$  is substituted for  $\text{Al}(\text{OEt})_3$ . Equations are given, and it is shown that the T. reaction and the Claisen reaction resulting in the formation of  $\text{PhCH}_2\text{OBz}$  can be interpreted analogously.

M. W. MCP.

**Synthetic rhodinol.** I. V. GRIGNARD AND R. ESCOURROU. *Bull. soc. chim.* 37, 542-5 (1925).—The results obtained in the hydrogenation of citral indicate that it might be possible to limit the hydrogenation of geraniol to double bond 2 and obtain the rhodinol of Barbier and Bouveault:  $\text{Me}_2\text{C}(\text{CHCH}_2\text{CH}_2\text{CMe}(\text{CHCH}_2\text{OH}) + \text{H}_2 = \text{Me}_2\text{C}(\text{CHCH}_2\text{CH}_2\text{CHMeCH}_2\text{CH}_2\text{OH})$ . Thirty g. geraniol gave a product  $b_p$  wholly  $107-8^\circ$ ,  $d_4$  0.8513,  $n_D^{20}$  1.45147, M. R. 49.38. Allophanate, m.  $111-15^\circ$ . Ozonization showed the product to be the  $\beta$ -form, with a trace of the  $\alpha$ -form:  $\text{CH}_3(\text{CMeCH}_2\text{CH}_2\text{CH}_2\text{CHMeCH}_2\text{CH}_2\text{OH})$ . Natural rhodinol and *dl*-rhodinol, synthesized by Bouveault and Gourmand, are the  $\beta$ -form. The rhodinol obtained by G. and E. was racemic, but was not identical with the rhodinol of B. and G., as indicated by the d. and b. p. Its const. were close to those of citronellol. The question of the relation between natural rhodinol and  $\beta$ -citronellol is still unsolved.

MARGARET W. MCPHERSON

**The selective hydrogenation of geraniol.** V. GRIGNARD AND R. ESCOURROU. *Bull. soc. chim.* 37, 546-8 (1925); cf. preceding abstr.—To accomplish the partial hydrogenation of geraniol, moist  $\text{Ni}$  and  $\text{H}$  were used. Fraction  $A_1$  (60 g. from 200 g.

geraniol)  $b_p$  116-8,  $n_D^{20}$  1.45137,  $d_4^{20}$  0.8516, most nearly identical with citronellol (Pt) (cf preceding abstr). Allophanate, m 112-3°; this m. p. is different from that of the other allophanate because each was a mixt. of the  $\alpha$ - and  $\beta$ -forms in different proportions. Ozonization did not distinguish between the relative proportions in the two cases because the precision of the method was not sufficient. Fraction A<sub>2</sub> (90 g. from 200 g. geraniol),  $b_p$  114.5-6.0°,  $n_D^{20}$  1.4463,  $d_4^{20}$  0.8420, was probably contaminated with the product from the hydrogenation of both double bonds. The hydrogenation of geraniol with Pt or Ni can be obtained in several phases and *dl*-citronellol can be obtained thus nearly quantitatively. MARGARET W. McPHERSON

New process for the production of sulfoxylate-formaldehyde. CH. SENDER AND CH. TROSSARELLI *Bull. soc. ind. Mulhouse* 91, 171-2 (1925).—Sealed Note No. 1903 of May 25, 1909. Addn. of bisulfite-formaldehyde to hyposulfite in presence of NaOH gives sulfoxylate-formaldehyde:  $Na_2S_2O_4 + NaHSO_3 \cdot CH_2O + 2NaOH = NaHSO_3 \cdot CH_2O + 2Na_2SO_3 + H_2O$ . In concd. soln., the  $Na_2SO_3$  crystals out, and the sepd. sol. is sufficiently concd. to discharge para-red. Report. MULLER GRISAN. *Ibid.* 172-3.—The reaction takes place according to the equation given by S and T, and not according to  $NaHSO_3 \cdot CH_2O + NaOH = Na_2SO_3 + CH_2O + H_2O$  and  $Na_2SO_3 + CH_2O + NaOH = NaHSO_3 \cdot CH_2O + Na_2SO_3$ . The process is of theoretical interest, but is not practical commercially. No priority was found. A. P. C.

Reducing action of organo-magnesium halides. HEINRICH RHEINHOLDT AND HANS ROSEFF. *J. prakt. Chem.* 109, 175-90 (1925); cf *C. A.* 19, 633; 16, 409.—The following % yields of  $PhCH_2CH_2OH$  were obtained from  $BzH$  and  $EtMgBr$  (I),  $C_6H_5MgBr$  (II) or *iso*- $BuMgBr$  (III) under the various conditions mentioned (for theoretical discussion see *C. A.* 19, 633) (the 2nd figure in each case is the ratio of reduction to normal product) in the cold: I, 8, 0.07; II, 13, 0.33. Addn. product heated in  $Et_2O$ : I, 11, 0.13; II, 20, 0.21; III, 40, 1.24. Addition product heated in  $C_6H_6$ : I, 16, 0.28; II, 53, 1.34. Addn. product heated in  $PhMe$ : I, 11, 0.21; in  $PhOMe$ : II, 21, 0.30.  $BzH$  added to Grignard reagent in boiling  $Et_2O$ : I, 31, 0.51; III, 44, 1.26.  $BzH$  added to Grignard reagent in boiling  $C_6H_6$ : I, 33.5, 0.67; III, 46, 1.37; in boiling  $PhMe$ : I, 14, 0.37. Grignard reagent added to  $BzH$  in  $Et_2O$ : I, 23, 0.47.  $EtBr$  added to  $Mg$  and  $BzH$  in  $Et_2O$ : I, 15, 0.43. Addn. product heated 2 hrs. in  $C_6H_6$ : I, 40, 0.72; 10 hrs., I, 24, 0.77. After standing 12 hrs., heated 2 hrs. in  $C_6H_6$ : I, 46, 0.63.  $C_6H_5MgCl + Ph_2CO$  in cold  $Et_2O$  give benzhydrol and  $C_6H_5CPh_2OH$ , m. 10°. Heating the addn. product from 15 g.  $C_6H_5MgCl$  and 22 g.  $Ph_2CO$  gives 5 g.  $C_6H_5CPh_2OH$ ;  $C_6H_5MgCl + C_6H_5COPh$  give *cyclohexylphenylcarbinol*, m. 83°,  $b_p$  209-12°, which does not show halochromism with concd.  $H_2SO_4$ ,  $HClO_4$ , or  $Cl_2CCO_2H$ . III and  $Ph_2CO$  gave only benzhydrol so that a quant. reduction occurred. III and *iso*- $BuCOPh$  at 13° gave only *iso*- $BuCPh_2OH$ . Pinacoln (20 g.) and III in the cold gave 5.8 g. pinacolyl alc. (IV), heating the addn. product in  $Et_2O$  gave the same yield of IV; adding it to the boiling  $Et_2O$  soln. of III gave 36% of IV. The addn. product of  $EtMgBr + BzH$ , treated with  $BzCl$ , gave 51% yields of *ethylphenylcarbinyl benzoate*,  $b_p$  183.5-4.5°. C. J. WEST

Electrolytic properties of organo-magnesium compounds. I. N. W. KONDYREW. *Ber.* 58, 459-62 (1925).—If 2 plates,  $Mg$  and  $Pt$ , are immersed in a soln. of  $EtBr$  in dry  $Et_2O$  and connected through a galvanometer, a current is indicated as soon as the  $Mg$  begins to go into soln. The resulting organo- $Mg$  compds. are typical electrolytes and different metals, immersed in such solns., show a p. d. Thus,  $Pt-Al$ , 0.73 v.;  $Pt-Mg$ , 0.76 v.;  $Pt-Cu$ , 0.02 v.;  $Pt-Fe$ , 0.2 v. In a colorless soln. of  $EtMgBr$  an anode of  $Mg$  and a cathode of  $Pt$  gave a current of 0.05 amp.; the resistance (15 ohms) remained const., indicating that the concn. of the soln. of  $EtMgBr$  remained const. The  $Mg$  deposited on the anode. In the case of a  $Zn$  anode and a  $Pt$  cathode, the resistance of the electrolyte increases with time.  $Mg$  deposits on the anode at first but is followed by  $Zn$ . With a  $Cu$  anode the current was 0.65 amp., the resistance 33-43 ohms; scarcely any  $Cu$  was dissolved from the anode and  $Mg$  deposited on the cathode. With  $Al$  anodes there is a gradual increase in the cond. of the soln.  $Al$  goes into soln., but  $Mg$  deposits on the cathode.  $PtMgBr$  with  $Pt$   $Mg$  gave 0.63 amp. and 35 ohms;  $PhMgBr$ ,  $Pt-Zn$ , 0.02 amp. and 42 ohms. II. Electrical conductivity of ethylmagnesium bromide in ether solutions. N. W. KONDYREW AND D. P. MAKOJEV. *Ibid.* 404-50.—The equiv. cond. increases with decreasing concn., the change being proportional to the sq. root of the diln. The values given are for  $N/1000$ ,  $r_{1000}$ ,  $\lambda_{1000}$ ,  $\lambda_{2000}$ : 0.0023, 0.434, 0.0776, 0.081, 0.099, 0.0014, 0.700, 0.121, 0.119, 0.108; 0.00071, 1.41, 0.167, 0.179, 0.136. For  $N/1000 = 0.002305$ , the temp. coeff. is positive, for the other concns. negative. C. J. WEST

Laboratory preparation of zinc diethyl and lead tetraethyl. MARTIN MEYER.

*Chem. News* 131, 1-2(1925).—Details of app and methods for the prepn of  $\text{ZnEt}_2$  and  $\text{PbEt}_4$  are given; yields, about 90%  $\text{ZnEt}_2$ , b  $118^\circ$ ,  $d_{25} 1.182$ ;  $\text{PbEt}_4$ , d 1.62.

C. J. WEST

The action of calcium hydride on some organic compounds. II. Methyl ethyl ketone and diethyl ketone. C PORCEZZA AND U GATTI. *Gazz chim. ital.* 55, 224-34 (1925).—The action of  $\text{CaH}_2$  on  $\text{Me}_2\text{CO}$  was previously described (*C. A.* 19, 35). The analogy in the behavior of  $\text{CaH}_2$ ,  $\text{Ca}(\text{OH})_2$  and  $\text{Ca}$  upon  $\text{Me}_2\text{CO}$  led P and G. to extend the expts to other homologs. The earlier work on the condensation of  $\text{MeCOEt}$  (I) is reviewed and the nomenclature of Ekeley and Howe (*C. A.* 17, 3479) is approved. Sixty-five g. I were treated with 16 g  $\text{CaH}_2$  in small portions while cooling the flask. After 37 days the mixt was extd with  $\text{Et}_2\text{O}$  and fractionated. The fraction, b  $163-7^\circ$ , was found to be pure homomestone (II),  $\text{EtMeC CHCOEt}$ . The higher fractions contained isomeric homophorones, which were shown to be analogous to those obtained by E and H., but which have not been fully characterized. As with  $\text{Me}_2\text{CO}$   $\text{Ca}$  caused the same action as  $\text{CaH}_2$  on I but was less efficacious. The condensing action of  $\text{CaH}_2$  on  $\text{Et}_2\text{CO}$  was scarcely appreciable. From the qual. point of view the expts. with  $\text{CaH}_2$  lead to the same result as that reported by Bodroux and Taboury (*C. A.* 2, 2949) from their expts. with  $\text{Ca}_2\text{C}$ ; i. e., that the condensation takes place in compds. contg. the  $\text{Ac}$  group. Among these compds. they include  $\text{MeCOPh}$ , the action of which with  $\text{CaH}_2$  is to be reported next.

E. J. WITZEMANN

Linolic acid and its anhydride. D. HOLDE AND R. GENTNER. *Ber.* 58B, 1067-71 (1925); cf. *C. A.* 17, 3619.—Linolic acid, prepd from the tetrabromide by Grün and Schönfeld's method (*C. A.* 10, 2210) and distd under 2 mm., has an i no. (Hanus) of 176-80,  $d_4^{25} 0.9038$ ,  $d_4^{25} 0.9007$ ,  $n_D^{25} 1.4715$ ,  $n_D^{25} 1.4683$ ,  $b_1 202^\circ$  (cor.); quickly cooled ( $\text{CO}_2$  snow) in a capillary in a m. p. bulb filled with alc., it solidifies about  $-25^\circ$ ; if, now, the m. p. bulb is placed in a freezing mixt at  $-7^\circ$  so that the temp rises rapidly from  $-25^\circ$  to  $-8^\circ$  but from  $-8^\circ$  to  $-7^\circ$  only slowly (about 10 min.) the acid m.  $-8^\circ$  to  $-7^\circ$ . When the pure acid in a small ampule in a bath at  $-15^\circ$  is stirred with a thermometer it deposits druse-like cryst nuclei and soon solidifies completely, the temp. rising spontaneously to  $-0.5^\circ$ ; this solid acid m. clear  $-0.5^\circ$  to  $-9.0^\circ$ . Linolic anhydride was prepd. by heating the acid with 3 times the calcd. amt. of  $\text{Ac}_2\text{O}$  in  $\text{CO}_2$  under a reflux 4-5 hrs. at  $150-70^\circ$ , removing the  $\text{Ac}_2\text{O}$  and  $\text{AcOH}$  in the vacuum of a  $\text{H}_2\text{O}$  pump at  $120-40^\circ$ , taking up in petroleum ether, shaking with  $\text{Na}_2\text{CO}_3$  and recrystg. the crude product (obtained in 91% yield) in an atm. of dry  $\text{CO}_2$  in an especially designed app., which is described. Quickly cooled in an alc. bath it solidifies  $-18^\circ$  and m.  $-1^\circ$  to  $-3^\circ$  when the temp is raised at the rate of  $2^\circ$  in 10 min.; its i no. is 177.2-8.5,  $d_4^{25} 0.901$ ,  $n_D^{25} 1.4775$ ,  $n_D^{25} 1.4737$ , mol wt in camphor 543.0.

C. A. R.

Addition products of iodine monobromide and hypoiodous acid with unsaturated compounds. I. D. HOLDE AND A. GORGAS. *Ber.* 58B, 1071-4(1925).—The  $\text{IBr}$  and  $\text{HOI}$  addn. products formed in the Hanus and Margosches methods, resp., of detg. I nos have thus far never been studied with any thoroughness. H and G have applied the 2 methods to 4 pure compds. with the following results, using a 50-80% excess of halogen (100% in the case of cholesterol (IV)). The values given below are the i nos. obtained with the M and the H method, resp. Oleic acid (I) 90.0-0.8, 89.1-9.5; erucic acid (II) 70.1-5.3, 74.0-4.6; linolic acid (III) (fresh) 176.3-6.4, 176.7; III (kept 3 months) 150.3-69.8, 169.6-70.9; IV, 0. — The addn. product obtained from II by the H. method is iodobromobehenic acid, m.  $38^\circ$ ,  $d_4^{25} 1.2479$ ,  $n_D^{25} 1.4922$ , stable to light and air in the solid state and in petroleum ether but decomps in  $\text{CHCl}_3$  and  $\text{Me}_2\text{CO}$ . The addn. product of III is diiododibromostearic acid, m.  $77.8^\circ$ . The product obtained by the M. method from I is iodohydroxystearic acid, faintly yellow viscous oil solidifying only at a very low temp (benzene- $\text{CO}_2$  snow),  $d_4^{25} 1.2070$ ,  $n_D^{25} 1.4962$ ; that from II is iodohydroxybehenic acid,  $d_4^{25} 1.1599$ ,  $n_D^{25} 1.4931$ ; that from III is diiododihydroxystearic acid, yellow-brown oil becoming deep brown after several days,  $d_4^{25} 1.369$ ,  $n_D^{25} 1.5195$ .

C. A. R.

Optical resolution of bromosulfoacetic acid. H. J. BACKER AND H. W. MOOK. *Verslag. Akad. Wetenschappen Amsterdam* 34, 87-8; *Proc. Acad. Sci. Amsterdam* 28, 63-6(1925).— $\text{HO}_2\text{SCHBrCO}_2\text{H}$  (I) was resolved by the method of "cold crystn." used for the chloro-acid (*C. A.* 19, 1128). Strychnine and brucine (II) were found most effective for obtaining the *d*- and *l*-forms, resp.; the use of II on the enriched soln. from isolation of *d*-I is recommended. The following nos. give the wave length (in  $\mu$ ) and

[M] for active 1 and its neutral  $\text{NH}_4$  salt, resp.: 589, 31°, 16°, 560, 37°, 18°; 533, 42°, 21°, 510, 47°, 21° 456, 56°, 27°. B. H. NICOLET

Sudden pyrogenic decomposition, at high temperature, of methylformate. MILLE ÉGLANTINE PEYRAL. *Bull. soc. chim.* 37, 562-8(1925); cf. *C. A.* 16, 2304, 2475.— $\text{HCO}_2\text{Me}$  (1.535 g.),  $b_{754}$  32.35°,  $d_{44}$  0.9781, passed as vapor through a 2-mm. Pt tube at 1150° gave 13 mg liquid  $\text{HCHO}$ , 340.5 mg.  $\text{HCHO}$  in soln., and 1103 cc. gas contg. per 100 vols.  $\text{CO}_2$ , 1.8,  $\text{HCHO}$  vapors, 0.6,  $\text{CO}$ , 53.0;  $\text{H}$ , 43.1;  $\text{C}$ , 4.1;  $\text{O}$ , 0.0;  $\text{CH}_4$ , 1.5. The  $\text{HCO}_2\text{Me}$  decomp. into 2 mols  $\text{HCHO}$ , the  $\text{HCHO}$  formed decomp. into  $\text{CO}$  and  $\text{H}_2$ , and the  $\text{HCHO}$  is partially hydrogenated to give  $\text{MeOH}$  as a limited secondary reaction. The decompn. of  $\text{HCO}_2\text{Me}$  is different from that of its isomer,  $\text{AcOH}$ , but comparable to that of its homolog,  $\text{AcOMe}$ . MARGARET W. McPHERSON

$\alpha$ -Ketoformhydroxamic acids and derivatives. X. C. GASTALDI. *Gazz. chim. ital.* 55, 201-14(1925).—This paper relates to 2 forms of benzoylformhydroxamic acid oxime (I). The  $\alpha$ -form (m 177°) is obtained from  $\text{NH}_2\text{OH}$  and benzoylformhydroxamic acid (II) (*C. A.* 18, 3172) and from  $\text{NH}_2\text{OH}$  and Et phenylglyoxylate (*C. A.* 19, 285). The  $\beta$  form is obtained by isomerizing the  $\alpha$ -form by heating with dil  $\text{AcOH}$  and from  $\text{NaHSO}_4$  and the oxime of the chloride of II (phenylchloroglyoxime) (*C. A.* 18, 3172). The  $\alpha$ -form differs from the  $\beta$  form in that it crystallizes in the monoclinic system or possibly in the triclinic, while the  $\beta$ -form is certainly rhombic. The behavior of the 2 forms toward  $\text{Ac}_2\text{O}$  is different. With  $\text{Ac}_2\text{O}$  in the cold the  $\alpha$ -form gives a tri-Ac deriv. (III),  $\text{PhC}(\text{NOAc})\text{C}(\text{NOAc})\text{OAc}$ , m 85°, and with heat a di-Ac deriv. (IV),  $\text{PhC}(\text{NOAc})\text{C}(\text{NOAc})\text{OH}$ , m 126°, and  $\text{PhCN}$ . On saponification with  $\text{NaOH}$  3 compds are formed: 3 phenyl 5-hydroxyfuro[ $a,b$ ]diazole (V), phenylhydroxyfuran (VI) and the  $\alpha$  form of I. The  $\beta$ -form with  $\text{Ac}_2\text{O}$  gives in the cold a tri-Ac deriv. (VII), m 117°, and with heat  $\text{PhCN}$ . When saponified VII gives the  $\beta$ -form of I and a trace of a compd. which is not V nor VI, but which may be phenylglyoxylic acid oxime. The  $\alpha$ - and  $\beta$  forms also behave differently toward  $\text{NaOH}$  and  $\text{EtONa}$ . With  $\text{NaOH}$  the  $\alpha$ -form gives the mono-Na deriv.  $\text{C}_6\text{H}_5\text{O}_2\text{N}_2\text{Na}$ ; with  $\text{NaOEt}$  it gives the di-Na deriv.  $\text{C}_6\text{H}_5\text{O}_2\text{N}_2\text{Na}_2$ . On heating the latter to 80-90° V and VI are formed. With  $\text{NaOEt}$  the  $\beta$  form gives a Na deriv.  $\text{C}_6\text{H}_5\text{O}_2\text{N}_2$ ,  $\text{C}_6\text{H}_5\text{O}_2\text{N}_2\text{Na}$ . The 2 forms also behave differently with  $\alpha$ - $\text{C}_6\text{H}_4(\text{NH}_2)_2$  (VIII). The  $\alpha$ -form reacts with VIII giving a compd.  $\text{C}_6\text{H}_5\text{O}_2\text{N}_2$ ,  $2\text{C}_6\text{H}_4(\text{NH}_2)_2$ , m 151°. With the  $\beta$ -form in the same conditions this compd. is not formed. Some further discussion of the mechanism of the formation of V is given. The details of all these preps. are given. At the end G. replies to the criticisms of Pozzo (*C. A.* 19, 2187). E. J. WITZMANN

Butyric. L. S. WEATHERBY, LILLIAN McILVAINE AND DAVID MATLIN. *J. Am. Chem. Soc.* 47, 2219-52(1925).—The rate of esterification of  $\text{C}_4\text{H}_9(\text{OH})_3$  and  $\text{PrCO}_2\text{H}$  with 1, 2, 3 and 6 mols. of acid is given; the excess of acid not only causes more complete esterification but in addition forces a greater yield of the insol. tributyrin. The ester has a characteristic, though not unpleasant odor, a markedly bitter taste, noticeable especially in the palate area of the throat;  $d_{20}$  1.027,  $b_{20}$  190°,  $n_D^{20}$  1.305-1.310; it begins to thicken at -35° and at -75° is so viscous that the thermometer could scarcely be withdrawn. C. J. WEST

Chemical nature of the fats. II. The periodine number of fatty oils and of unsaturated fatty acids with the same iodine number. B. M. MARGOSCHES, LUDWIG FRIEDMANN, ERWIN SCHEINOST AND WALTER TSCHÖRNER. *Ber.* 58B, 1064-7(1925); cf. *C. A.* 19, 2326.—By the technique described in the 1st paper (the titration of the I with  $\text{Na}_2\text{S}_2\text{O}_3$  is facilitated by adding a few cc.  $\text{CCl}_4$  towards the end), the periodine nos. of a no. of pairs of oils having approx. the same I no. were detd. Below are the I and P. I. nos., resp., of the different oils: olive 84.3, 119.7; castor 87.7, 162.2; rape seed 100.1, 142.2; almond 101.5, 147.5; cottonseed 109.1, 139.0; sesame 109.2, 145.4; sunflower 133.9, 185.6; poppy-seed 133.6, 198.1. Mixts. of olive and castor oils, contg. 24.32, 51.88 and 73.22% castor oil gave P. I. nos. of 128.2, 139.6 and 152.7, the calcd. values being 130.0, 141.7 and 160.5, resp.; the compn. of such mixts. can therefore be detd. with an accuracy of about 5% by means of their P. I. nos. The error is smaller the greater the concn. of the olive oil, pointing to an influence of the HO groups. The influence of HO groups was also shown by a study of grape-seed oil, the results for which are given in the form of a curve. The differing behavior of 2 unsatd. fatty acids with the same I no. (9,10-oleic and 9,10-elaidic) is also shown by means of curves. Whereas with the former the reaction proceeds as given in the 1st paper ( $\text{RCH}=\text{CH}(\text{OH})\text{R}' + \text{HOI} \rightarrow \text{RCHICH}(\text{OH})\text{R}'$ , and  $\text{RCH}=\text{CH}(\text{OH})\text{CH}=\text{CH}\text{R}'' + \text{HOI} \rightarrow \text{RCHICH}(\text{OH})\text{CHICH}(\text{OH})\text{R}''$ ), with the latter the reaction after satn. of the double bonds proceeds according to the scheme  $\text{RCHICH}(\text{OH})\text{R}' + \text{H}_2\text{O} \rightarrow \text{RCH}(\text{OH})\text{CH}(\text{OH})\text{R}' + \text{HI}$ . C. A. R.

$\alpha$ -Ethyl- $\alpha$ , $\alpha'$ -thiodilactylic acid. R. AHLBERG. *Ber.* 58B, 1061-2(1925).—The  $\alpha$ -ethyl- $\alpha$ , $\alpha'$ -thiodilactylic acid (I) required for a study of the convertibility of the  $\text{SO}_2$  group into the enol form (*C. A.* 18, 2497) was obtained in good yield from  $\text{MeCH}(\text{SNa})\text{CO}_2\text{Na}$  and  $\text{EtCBrMeCO}_2\text{Et}$ . Since it contains 2 non-equiv. asym. C atoms, it must exist in 2 *dl*-forms, in the isolation of which, however, difficulties were at once encountered. To be sure, about 0.5 of the acid crystals, out and a pure *dl*-form (II), m.  $133^\circ$ , can be obtained from it through the acid K salt, but no pure product can be obtained from the mother liquors. With brucine it is possible almost completely to isolate II, and the mother liquors of the brucine salt yield, through the acid K salt, a lower melting product consisting of 2 other forms, the relative amts. of which differed in different syntheses. One (III) m.  $93^\circ$ , the other (IV) (probably not quite pure)  $86-9^\circ$ . They resemble each other very closely, the most striking difference being in their acid cinchonidine salts, that of IV crystals well while that of III is an oil. The ester acid obtained in the prepn. of I and its isomers boils within a temp. interval of  $15-20^\circ$  and no const. b. p. can be obtained by repeated distn., this temp. interval can be shifted by about  $10^\circ$  by using the  $\text{MeCH}(\text{SH})\text{CO}_2\text{H}$  in about 10% excess with respect to the Na. Besides II-IV, a 4th form, similar in soly and m. p. to II, has probably been discovered. Since I therefore probably exists in 4 different inactive forms, all of which again are probably *dl*-forms, there are apparently 12 different forms of I, whose isolation and characterization will prove a difficult task. C. A. R.

Aldehyde compounds of the amino acids. MAX BERGMANN, HELMUT ENSSLIN AND LEONIDAS ZERVAS. *Ber.* 58B, 1034-43(1925).—Aldehydes and salts of the  $\text{NH}_2$  acids in  $\text{H}_2\text{O}$  readily give in almost all cases the pure *N*-aldehyde-amino acid salts of the type  $\text{RCH:NCHR}'\text{CO}_2\text{M}$  ( $\text{MO}_2\text{CCH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{M}$  in the case of asparaginic acid); peptides (glycylglycine) behave similarly. Ba and Ca were at first mostly used as the metal because their hydroxides are sufficiently sol. to form salts rapidly with the  $\text{NH}_2$  acids in  $\text{H}_2\text{O}$  while, on the other hand, they usually become sufficiently difficultly sol., after introduction of the aldehyde component, to be recrystd. from  $\text{H}_2\text{O}$  or aq. alc. With alkali-sensitive compds. the acetate of the metal can often be used instead of the hydroxide. The metal salts of the aldehyde amino acids, however, frequently have but a slight tendency to cryst. and attempts were made to substitute org. N bases for the metals. Brucine has given good results in a no. of cases. The simplicity of the operations is of importance as it affords a new analytical means for the isolation and identification of  $\text{NH}_2$  acids and peptides. The  $\text{NH}_2$  acids can easily be regenerated from the aldehyde compds. and, moreover, the basic component can be removed and replaced by acid residues with the formation of derivs. having convenient phys. properties (sharp m. p., etc.). In some cases the aldehyde-amino acid salts have been obtained in 2 different cryst. forms, but as they are infusible substances which cannot readily be recrystd., they have not yet been sep'd. and it has not been possible to decide whether they are the theoretically possible stereoisomers. *N*-Benzylideneglycine: Ba salt,  $(\text{PhCH:NCH}_2\text{CO}_2)_2\text{Ba}$  (1.7 g. from 2.1 g. crystd.  $\text{Ba}(\text{OH})_2$  and 1 g. glycolol in 4 cc. hot  $\text{H}_2\text{O}$  quickly cooled, treated at once with 1.4 g.  $\text{BzH}$  and shaken vigorously), 4 cc. hot  $\text{H}_2\text{O}$  quickly cooled, smells strongly of  $\text{BzH}$  in moist air, being gradually decomp'd. by seps. with  $4\text{H}_2\text{O}$ , more rapidly on heating; Ca salt; Ac deriv. (cl. Scheibler and Baumgarten, *C. A.* 16, 3879; B., E. and Z. give the preference to the 2-phenyl-3-acetyl-5-oxazolidone structure for this comp'd.), from the Ba salt and  $\text{AcO}$  in boiling  $\text{C}_6\text{H}_5\text{N}$ , b.  $210-20^\circ$  (bath temp.), m.  $103.5^\circ$  (cor.); Bz deriv. (2-phenyl-3-benzoyl-5-oxazolidone), from the Ba salt and  $\text{BzCl}$  in boiling  $\text{CCl}_4$ , m.  $134.5-50^\circ$  (cor.). Ba *N*-*o*-hydroxybenzylideneglycine (1.1 g. indistinctly cryst. product from 0.5 g. glycolol, 1.1 g. crystd.  $\text{Ba}(\text{OH})_2$  and 0.8 g. *o*- $\text{HOC}_6\text{H}_4\text{CHO}$  in 25 cc.  $\text{H}_2\text{O}$  at  $-5^\circ$ , or 0.95 g. pure, well crystd. product from 0.5 g. glycolol, 1.4 g. crystd.  $(\text{AcO})_2\text{Ba}$  and 1.2 g.  $\text{HOC}_6\text{H}_4\text{CHO}$  in 3 cc.  $\text{H}_2\text{O}$  and 6 cc. of 50% alc.), lemon-yellow microleaflets. Ba *N*-furfurylideneglycine (1.1 g. from 1 g. glycolol), yellowish, retains 1  $\text{H}_2\text{O}$  after drying under 2 mm over  $\text{P}_2\text{O}_5$ . Ba *o*-hydroxybenzylidene-*dl*-phenylalanine (0.37 g. from 0.85 g. phenylalanine), yellow. Ba *N*-benzylidene-[*N*-glycylglycine] (0.34-0.4 g. from 0.35 g. glycylglycine); *o*-hydroxybenzylidene analog (0.47 g. from 0.25 g. of the peptide), lemon-yellow. Ba *N*-*o*-benzylidene-*L*-asparaginate (0.2 g. from 0.65 g. of the  $\text{NH}_2$  acid), yellow; dibrucine salt (2 g. from 0.3 g. of the  $\text{NH}_2$  acid, 2.1 g. hydrated brucine and 0.3 g.  $\text{HOC}_6\text{H}_4\text{CHO}$  in 25 cc. of 20% alc.), lemon-yellow prisms or tables losing 14.74-15.06% in wt. at  $78^\circ$  under 1 mm. over  $\text{P}_2\text{O}_5$ , m. (anhyd.)  $145^\circ$  (foaming), quickly dissolves in 20 parts cold  $\text{MeOH}$ , but there soon sep. faintly yellow microneedles contg. only 1 mol brucine; analysis indicates that  $\text{MeOH}$  has also been taken up. Dibrucine *N*-*p*-nitrobenzylidene-*L*-asparaginate (1.8 g. from 0.3 g. of the  $\text{NH}_2$  acid), pale yellow, becomes reddish yellow at  $20^\circ$  under 0.5 mm. over  $\text{P}_2\text{O}_5$ , and deep red at  $78^\circ$  but  $\text{H}_2\text{O}$  restores the yellow color,

sinters 95° m around 116° (foaming). Dibrucine *N*-trichloroethylideneasparaginate (yield 60%), loses 11.43% in wt. at 78° under 0.5 mm over  $P_2O_5$ . *Bz N*- $\alpha$ -hydroxybenzylidene *d* glutaminate (0.7 g from 0.35 g of the  $NH_2$  acid), yellow, loses 12.98–13.12% in wt. at 78° under 1 mm over  $P_2O_5$ , quickly develops the odor of  $\alpha$ - $HOC_2H_4$ -CHO with hot dil.  $H_2SO_4$ , gives a yellow-brown ppt. with  $AgNO_3$ ; dibrucine salt (2.1 g from 0.5 g of the  $NH_2$  acid), lemon-yellow, m. 148° (foaming). C. A. R.

**Oganomagnesium compounds.** The reaction between magnesium and acid halides. D. V. TISTCHENKO *Bull. soc. chim.* 37, 623–37 (1925).— $AcBr$  in 6 vols. of  $Et_2O$  reacts slowly with  $Mg$  at the b. p. of the mixt., the final products being 35% of  $AcOEt$  and 30% of  $Ac_2O$ ; if no solvent is used the reaction is violent and the product poorly defined.  $Me_3CHCH_2COBr$  (I) with  $Mg$  in  $Et_2O$  gives, after decompn. with  $HCl$ , 27%  $Me_3CHCH_2CHO$  (II), 40%  $Me_3CHCH_2CH:C(CHMe_2)CHO$  (III), 15% of isovaleron isovalerate (IV) and 7% of disovaleryl (disobutylacetyleneglycol disovalerate) (V). Since the 1st 2 fractions total 70% of the yield it is evident that the  $Mg$  deriv. of I has the normal structure  $Me_3CHCH_2COMgBr$ .  $Me_3CHCOBr$  (VI) reacts with  $Mg$  to give as final products 30% of isobutyron (VII), 30% of the isobutyrate of VII, and 5% of disobutyl (VIII). The simple  $Mg$  compd. of VI apparently doubles up to form  $Me_3CHC(OMgBr)(MgBr)COCHMe_2$ , which with  $H_2O$  gives VII, the main reaction product.  $BzBr$  with  $Mg$  in  $Et_2O$  gave as final products only  $BzOH$  and resins. The reaction of the  $Mg$  compds. of  $AcBr$ , I, and VI with various compds. has been studied;  $CO_2$ ,  $HCO_2Et$ ,  $Me_2SO$ ,  $Ac_2O$ ,  $BzH$ ,  $PhCH_2Cl$ ,  $EtI$ ,  $AmBr$ , and  $PhBr$  did not react,  $s$ , subsequent decompn. with  $H_2O$  gave the same products previously noted. If 1 mol. of I be added to 1 mol. of its  $Mg$  compd. in  $Et_2O$ , decompn. gives 22% of  $Et$  isovalerate, 42% of V, 12% of IV.  $COCl_2$  reacts vigorously with these acyl  $Mg$  compds. but the expected triketones could not be isolated, the products being completely resinous. With  $Br$  the  $Mg$  compd. of I reacts to give, after decompn., 25% of  $Et$  isovalerate, 25% of  $EtBr$ , and 30% of V;  $(COBr)_2$  evolves  $CO_2$  but otherwise gives the same effect as  $Br$ . Consists of the various fractions above follow (approx. for the only partly purified, reaction products proper); III  $b_{10}$  85–7°,  $b_{100}$  187–9°,  $d_{20}^{20}$  0.848, absorbing  $O$  so rapidly as to prevent complete purification for analysis; V  $b_{10}$  170–3°, VII  $b_{100}$  140–54°,  $d_{15}^{15}$  0.910 (its osazone m. 130.5–40°), IV  $b_{10}$  133–5°,  $d_{10}$  0.913; VIII  $b_{10}$  130–40°; the disobutyrate of VII  $b_{10}$  91–4°,  $b_{100}$  210–8°,  $d_{15}^{15}$  0.911. Wm. B. PLUMMER

**Hepto- and nono-dilactones.** G. M. BENNETT *J. Chem. Soc.* 127, 1277–82 (1925).—Heptodilactone (I) (the dilactone of  $(HIOCH_2CH_2)_2C(CO_2H)_2$ ) is obtained in 5–10% yields from  $CH_3(CO_2Et)_2$  with  $EtONa$  and  $CICH_2CH_2OH$ ,  $BrCH_2CH_2OH$ ,  $CICH_2CH_2OAc$ ,  $BrCH_2CH_2OAc$  or  $p$ - $O_2NC_6H_4CO_2CH_2CH_2Cl$  in  $EtOH$ . Poor yields of I were obtained from  $CICH_2CH_2OH$  or  $(CH_3)_2O$  and the  $Na$  deriv. of  $Et$  butyrolactonecarboxylate or from  $EtONa$  and di- $\beta$ -chloroethyl malonate,  $b_D$  164°.  $Et$   $\beta$ , $\beta'$ -dimethoxydiethylmalonate,  $b_D$  153°, results from  $CH_3(CO_2Et)_2$  and  $MeOCH_2CH_2I$  (II) and gives a 40% yield of I by boiling with concd.  $HCl$ , but the poor yield of II makes the method of little practical value. Benzyl  $\beta$ -hydroxyethyl ether,  $b_D$  138°, results in 166 g yield from 300 g.  $(CH_3OH)_2$ , 37.5 g.  $Na$  and 225 g.  $PhCH_2Cl$ , 16 g. in 13 g.  $PhNMe_2$  with 14.5 g.  $SOCl_2$  give 13 g. benzyl chloroethyl ether,  $b_D$  124°,  $d_4^{20}$  1.109,  $n_D^{20}$  1.5201.  $CH_3(CO_2Et)_2$ , followed by hydrolysis, gives  $\beta$ , $\beta'$ -dibenzoyloxydiethylmalonic acid, m. 120°, which gives 45–50% I with fuming  $HBr$ . Nonodilactone (III) was prepd. by boiling  $(CH_3)_2CHCH_2C(CO_2Et)_2$  with 3 vols. 70%  $H_2SO_4$ . With  $KOBr$  it yields  $CHBr_3$ , thus proving the  $\gamma$ -lactone formula. I crystals in trigonal crystals having the Millerian axial angle of  $127^\circ 18'$  (Bravais-Miller axial ratio  $a:c = 1:2.002$ );  $c$  (111),  $r$  (100);  $\epsilon$  73° 23',  $\epsilon_r$  112° 15'. The crystals are uniaxial with positive double refraction;  $d_4^{24}$  1.541;  $\omega$  1.552;  $\epsilon$  1.588. III is tetragonal,  $a:c = 1:1.710$ ;  $\epsilon$  (001),  $r$  (101),  $s$  (201),  $m$  (110);  $\epsilon$  59° 41',  $\epsilon_r$  73° 37',  $\epsilon_s$  85° 30';  $d_4^{16}$  1.321;  $\omega$  1.494,  $\epsilon$  1.571. C. J. West

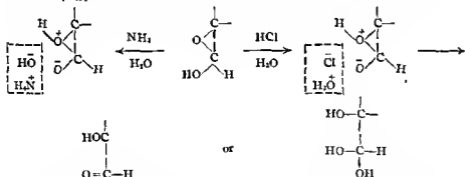
**Mucic acid.** EUGENE KNOTINSKY AND MME. T. EPFANOWA. *Bull. soc. chim.* 37, 544–51 (1925).—The crude product of the neutralization of mucic acid with  $MeNH_2$  yields on distn. principally *N*-methylpyrrolcarboxylic methylamide (I) and relatively little *N*-methylpyrrole (II). Pure  $MeNH_2$  mucate, however, yields principally II with I as a secondary product. The first result occurs because some of the mucic acid forms a monolactone before neutralization and the lactone forms with  $MeNH_2$  a salt of methylmucinic acid,  $MeNHCO[CH(OH)]_2CO_2H.NH_2Me$ , which was prepd., analyzed, and found to give, on dry distn., a fuger yield of I than does pure  $MeNH_2$  mucate. The distn. of mucic acid by titration with alkali was found to give uncertain results, for mucic acid, unlike certain HO acids which require more than the theoretical quantity of alkali, requires less than the theoretical. Titration, however, was used to det. the

amt. of lactonization of mucic acid at 56°. In the prepn. of Na mucate by the method of E. Fischer, a ppt. of anhyd. Na mucate was formed in the clear soln. of mucic acid in 2 mols. *N* NaOH, before the acid had completely dissolved. This is contrary to F.'s result. F. used freshly prepd. mucic acid and K. and E. did not. They have no explanation for this difference.

**The mechanism of oxidation of thymine.** 4,5-Dihydroxyhydrothymine (thymine glycol). OSKAR BAUDISCH AND DAVID DAVIDSON *J. Biol. Chem.* 64, 233-9 (1925).—4,5-Dihydroxyhydrothymine (thymine glycol),  $C_5H_8N_2O_4$ , from 5 biomo-4-hydroxythymine (Jones, *Z. physiol. Chemie* 29, 20 (1899-1900)) and moist  $Ag_2O$ , decomps 220°. Hydrolysis with  $NaHCO_3$  yields acetole and urea,  $Ba(OH)_2$  yields acetole, urea and 1 mol.  $CO_2$ . Reduction with  $Hf$  yielded thymine, showing persistence of the pyrimidine ring in the oxidized compd. Oxidation with Na pentacyano-aquo-ferrate and  $O_2$  yielded  $AcCO_2H$ .

**Alkylallylbarbituric acids.** E. H. VOLWILER *J. Am. Chem. Soc.* 47, 2236-40 (1925).—The following derivs were prepd by the usual methods. All b or m. ps. are corrected. The 2nd figure is the yield. Derivs of *Et malonate*: *Et*,  $b_{735}$  207-9°, 80; *Pr*,  $b_{734}$  222-7°, 75; *iso-Pr*,  $b_{731}$  215-7°, 60; *Bu*,  $b_{710}$  242-5°, 70; *iso-Bu*,  $b_{710}$  212-27°, 55; *sec-Bu*,  $b_{723}$  245-50°, 75; *iso-Am*,  $b_{741}$  245-50°, 75. Derivs. of *barbituric acid*: *Et*, m. 193-4°, 80; *Pr*, m. 204.5-5.5°, 70; *iso-Pr*, m. 214-4.5°, 50; *Bu*, m. 208-9°, 60; *iso-Bu*, m. 235-6°, 50; *sec-Bu*, m. 197-9°, 70; *iso-Am*, m. 242°, 45. **Alkylallylbarbituric acids**: *Et*, m. 158-9.5°, 75; *Pr*, m. 133-4.5°, 72.5; *iso-Pr*, m. 137.5-8.5°, 82; *Bu*, m. 128°, 73; *iso-Bu*, m. 137-8.5°, 82; *sec-Bu*, m. 108-10°, 72; *iso Am*, m. 118-9.5°, 66. Their physiol. actions have been compared with those of known dialkylbarbituric acids. Tests on white rats show that the alkylallylbarbituric acids fall in the following order of decreasing desirability as hypnotics, based upon their efficiency and toxicity: *Bu*, *iso-Bu*, diallyl, *Pr*, *iso-Pr* or *sec-Bu*, *iso Am*, *Et*. Values are given for the min lethal dose and min. effective dose.

**Dynamic Isomerism. XVIII. Mechanism of mutarotation.** T. M. LOWRY, *J. Chem. Soc.* 127, 1371-85 (1925).—Thus is a reply to the assertion of Baker, Ingold and Thorpe (*C. A.* 18, 972) that  $H_2O$  "does not intervene" in the mutarotation of the sugars. The initial stage in the conversion of the oxidic into the aldehyde form of the sugar is formulated as depending on the combination of the sugar either with base +  $H_2O$  or with acid +  $H_2O$  as in the scheme:



This mechanism is put forward as a natural development, in view of the clearer conceptions of the electronic theory of valency, of the fundamental hypothesis (*J. Chem. Soc.* 75, 213 (1899)) that the mutarotation of the sugars is due to a reversible isomeric change and of the subsidiary hypothesis (*Ibid* 83, 1316 (1903)) that this change proceeds through an intermediate aldehydic phase; it also embodies Armstrong's "oxonium" formula for the hydrate of  $\alpha$ -glucose (*Ibid* 83, 1309) and the formulation of hydrolysis as an isomeric change following the addn. of  $H_2O$  (*Ibid* 84, 1567 (1904)). It appears to cover all the essential points raised by B., I. and T., but goes beyond the point that was reached in the 1899 or 1924 papers, in that it not merely attributes mutarotation to isomeric change, but also assigns a definite part to those chem. agents without which, it appears, mutarotation cannot proceed. In this way it removes some of the vagueness which attaches to the use of the terms "tautomerism" and "catalysis" in connection with the phenomena of mutarotation, since these terms have served hitherto mainly as a cloak to conceal our ignorance of the method of action of these essential chem. agents, although their importance has long been obvious. XIX. Experiments on the arrested

mutarotation of tetramethylglucose. T. M. LOWRY AND E. M. RICHARDS. *Ibid* 1385-401.—Although alucose is unsuitable for use in expts on the arrest of mutarotation, the tetramethylglucose of Purdie and Irvine is an ideal sugar for this purpose, on account of its ready soly in anhyd. solvents and of the possibility of adequate purification by crystg it from such solvents. The mutarotation in  $\text{CHCl}_3$  was (in 1 instance only) arrested during a period of 10 days, just as was formerly observed in the case of nitrocamphor, this arrest is attributed to the elimination of catalysts by  $\text{COCl}_2$  derived from the  $\text{CHCl}_3$  by oxidation. The velocity of mutarotation in  $\text{C}_6\text{H}_6$  was reduced from 0.0008 to 0.0001 by careful drying, but a very rapid mutarotation was produced by the addn of  $\text{H}_2\text{O}$ , this was attributed to the possible presence in the  $\text{C}_6\text{H}_6$  of  $\text{H}_2\text{O}$ -sol impurities which developed strong catalytic properties only after association with  $\text{H}_2\text{O}$ . The mutarotation in  $\text{AcOEt}$  was preceded by a period of induction extending over about a day, this solvent, therefore, appears to possess no catalytic property of its own in the absence of an auxiliary catalyst. In presence of small quantities of  $\text{H}_2\text{O}$ , mutarotation proceeded without a period of induction. No arrest or period of induction was observed in the mutarotation of glucose in  $\text{MeOH}$  or of tetramethylglucose in  $\text{MeOH}$  or  $\text{EtOH}$ . It is therefore possible that  $\text{MeOH}$  is a real catalyst for the mutarotation of the sugars, although 30 times less efficient than  $\text{H}_2\text{O}$ . But this view is based only on negative evidence, since it is possible that further purification may reduce (or even eliminate) the small residue of catalytic activity which it appears to possess. The velocity of mutarotation in  $\text{C}_6\text{H}_5\text{N}$ , to which no  $\text{H}_2\text{O}$  has been added, is very small, but no arrest of mutarotation has yet been recorded. The mutarotation of tetramethylglucose in  $\text{C}_6\text{H}_5\text{N}$ , however, was preceded by a short period of induction; this shows that the change is not spontaneous but depends upon the presence of an auxiliary catalyst. A clear distinction is drawn between inactive solvents, such as  $\text{CHCl}_3$ , which have no catalytic properties, ampholytic solvents such as  $\text{H}_2\text{O}$ , which can act as complete catalysts; solvents such as  $\text{C}_6\text{H}_5\text{N}$ , which are not catalysts when pure, but develop catalytic properties in the presence of an auxiliary catalyst; the mixed catalysts formed in this way are more efficient than the complete catalysts, and often give rise to a mutarotation which is too fast to be followed experimentally. C. J. WHEAT

The condensation of monosaccharides by means of dilute mineral acids. P. A. LEVENE AND R. ULFS. *J. Biol. Chem.* 64, 475-83 (1925).—When solns of chitose, chondrose, glucose, mannose or lyxose, contg  $\text{HCl}$  were evapd, *in vacuo*, with or without the later addn and evapn of  $\text{EtOH}$ , yellow resins were obtained. These had little or no reducing action. Boiling with dil acids yielded the original sugars. Condensation product from chitose, insol in the usual solvents, has a reducing action 6% of that of glucose, instead of 81% with chitose. Condensation product from chondrose,  $[\alpha]_D^{20}$  20.8°; its reducing action is 13% that of glucose, instead of 55% with chondrose, mol. wt 351. Condensation product from glucose, has a reducing action 9.3% that of glucose,  $[\alpha]_D^{20}$  93°, mol. wt 351. Condensation product from mannose,  $[\alpha]_D^{20}$  59.5° did not reduce Fehling soln.; mol. wt 378. Condensation product from lyxose,  $[\alpha]_D^{20}$  41.5°, mol. wt 338. I. GREENWALD

Monoacetone-galactose. P. A. LEVENE AND G. M. MEYER. *J. Biol. Chem.* 64, 473-4 (1925).—The sirup of diacetone-galactose obtained by the method of Svanberg and Sjöberg (*C. A.* 17, 2703) was allowed to stand at room temp. during the summer months. Crystn. was found to have begun at several points. The sirup was stirred with  $\text{Et}_2\text{O}$  and kept at  $-10^\circ$  for several months. Crystn. had progressed and was hastened by the addn of baron. After filtering and recrystg twice from  $\text{EtOAc}$  and ligroin, the substance was pure. Monoacetone-galactose,  $\text{C}_7\text{H}_{12}\text{O}_6$ , in  $157^\circ$ ,  $[\alpha]_D^{20} = -10.9^\circ$  (in  $\text{EtOH}$ ). It does not reduce Fehling soln. nor is it oxidized by the hypiodite method of Willstätter and Schudel (*C. A.* 13, 406). I. GREENWALD

$\gamma$ -Galactan contained in the seeds of *Cicer arietinum* and its molecular constitution. N. CASTORO. *Ann. chim. applicata* 15, 146-55 (1925).—The method for extg.  $\gamma$ -galactan from the seeds of *Cicer arietinum* which has already been described (*C. A.* 5, 512) can be improved if, instead of pptg. the  $\gamma$ -galactan with abs  $\text{EtOH}$ , the soln. is treated with a boiling satd.  $\text{Sr}$  soln. The latter pptg. the saccharose which is otherwise difficult to remove from the  $\gamma$ -galactan. Reducing sugars also present as impurities are then removed by boiling the  $\gamma$ -galactan repeatedly with 90%  $\text{EtOH}$  and pptg. with 95%  $\text{EtOH}$  until a negative Fehling reaction is obtained. The product can be still further purified by dissolving in a min. amt. of  $\text{H}_2\text{O}$ , adding enough  $\text{HCl}$  to make the soln. 90%  $\text{EtOH}$  and then pptg. with 95%  $\text{EtOH}$ , repeating at least 3 times. The purified  $\gamma$ -galactan, for which the name *cicerose* is proposed, is very hygroscopic, is wholly insol. in abs.  $\text{EtOH}$ , is extremely sol. in  $\text{H}_2\text{O}$ , does not react with  $\text{PhNHNH}_2$ , and  $\text{HOAc}$  and

does not reduce Fehling soln. unless it is first hydrolyzed with mineral or org. acids, in which case it reduces it actively, the hydrolyzed product then giving with  $\text{PhNHNH}_2$  and  $\text{HOAc}$  a *glucosazone*, yellow-orange, m. 204–5°. Oxidized with  $\text{HNO}_3$  (d. 1.15) cicerose gives 38% of mucic acid and a small quantity of saccharic acid, and heated with  $\text{HCl}$  and resorcinol it gives the Selivanov reaction (cf. *Ber.* 20, 181(1887)). A study of the exptl. results, which include polarimetric measurements of the purified cicerose and its reaction products, excludes the possibility of its being a monose, a disaccharide or a trisaccharide, its properties and reactions limiting it to a tetrose of the type of lupoese. On the latter assumption, further reactions were carried out, including hydrolysis by  $\text{H}_2\text{SO}_4$  and isolation of the reaction products according to recognized methods. In this way it was finally proved that cicerose is a tetrasaccharide composed of 2 mols. of galactose, 1 mol. of glucose and 1 mol. of fructose  $\text{C}_6\text{H}_{12}\text{O}_6 + 3\text{H}_2\text{O} \rightarrow 2 \text{ d-galactose} + \text{d-glucose} + \text{d-fructose}$ .

C. C. DAVIS

**Composition of starch iodide.** H. D. MURRAY. *J. Chem. Soc.* 127, 1288–94 (1925).—The compn. of starch iodide was studied by detg. the concns. of free and combined I in the resultant soln. when I dissolved in  $\text{CCl}_4$  is shaken with a soln. of starch contg. a known amt. of KI. In order to calc. the concn. of the tri iodide ion, the equil. concn. of the iodide ion was measured by means of an I electrode. It is suggested that an addn. compd. is formed by the starch, the anion of which, in dil. KI solns., has the formula  $(\text{C}_6\text{H}_{10}\text{O}_5)_n\text{I}'$ , where  $n$  is approx. 15. At higher iodide concns., the iodide ion is taken up in excess of the requirements of this compd., pointing possibly to the formation of  $(\text{C}_6\text{H}_{10}\text{O}_5)_n\text{I}_2'$  and even of  $(\text{C}_6\text{H}_{10}\text{O}_5)_n\text{I}_3'$ .

C. J. WEST

**Spatial structure of cycloparaffins. I.** A new aspect of Mohr's theory and the isomerism of decahydronaphthalene. W. A. WIGHTMAN. *J. Chem. Soc.* 127, 1421–4 (1925).—A discussion of whether coördinated relative rotations about the single bonds are possible without strain and the examn. of the consequences of such a phenomenon. Models in which these mechanical requirements are fulfilled are shown. C. J. WEST

**Conditions underlying the formation of unsaturated and cyclic compounds from halogenated open-chain derivatives. VII.** The influence of the phenyl group on the formation of the cyclopropene ring. WILHELM HAERDI AND J. F. THORPE. *J. Chem. Soc.* 127, 1237–48 (1925).—An attempt was made to prep. the acid I which, in its semi-aromatic form, would have the structure II, in order to supply further evidence in support of reported views regarding the structure of the semi-aromatic ring type of which the acid III is at present the only known member. I was not obtained but the effect of the Ph group on 3-C ring formation was studied.  $\text{PhCH}(\text{CH}_2\text{CO}_2\text{H})_2$ ,  $\text{PCl}_5$  and Br, warmed for 2 hrs. and then poured into MeOH gave *Me* a *bromo-β-phenylglutarate* (IV), b<sub>p</sub> 204–6°, m. 86–7°, larger amts. of Br gave the α,α'-di-Br deriv., b<sub>p</sub> 215–20°, m. 82.5–3.5°, whose *Et* ester (V) is a viscous liquid. The free acid m. 192–3°. Distn. of V *in vacuo* gives the lactone of *Et* α-bromo-α'-hydroxy-β-phenylglutarate, (VI), b<sub>p</sub> 230–4°. Hydrolysis of IV gave  $\text{PhCH}(\text{CH}_2\text{CO}_2\text{H})_2$ , when MeOH-KOH was used, or the *Me* ester when  $\text{C}_6\text{H}_5\text{N}$  was used. V (or the *Me* ester) and MeOH-KOH did not give the expected I but a mixt. of 10%  $\text{PhCH}(\text{CHCO}_2\text{H})_2$  and  $(\text{CO}_2\text{H})_2$  and 2-ethoxy-3-phenylcyclopropane-1,2-dicarboxylic acid, m. 198–9°, stable towards alk.  $\text{KMnO}_4$  for 24 hrs. *Me* ester, b<sub>p</sub> 175–9°; *Et* ester, b<sub>p</sub> 184–90°. VI gave the same products but the  $\text{PhCH}(\text{CHCO}_2\text{H})_2$  and  $(\text{CO}_2\text{H})_2$  were present in larger amts. *Me* 1-bromo-3-phenylcyclopropane-1,2-dicarboxylate (VII), oil which solidifies in a freezing mixt.; the *Br* acid ester m. 175–6°. The bromination proceeds in the absence of a catalyst but in the light

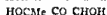


of an arc-lamp at 125–40°. Dibromination gave a product,  $\text{C}_{11}\text{H}_9\text{O}_4\text{Br}^?$ , m. 227–8°, which may be a Br-acid or a bromolactonic acid. Hydrolysis of these esters gives phenylcyclopropanedicarboxylic acid, m. 175–6°. *Et* α-carbethoxy-α'-bromo-β-phenylglutaconate, on hydrolysis with aq. KOH, gives 60–70%  $\text{BzCH}_2\text{CH}(\text{CO}_2\text{H})_2$ ; in EtOH the hydrolysis gives  $\text{BzCH}_2\text{CH}_2\text{CO}_2\text{Et}$ ; after standing 2 days with EtOH-NH<sub>3</sub> a compd. contg. both N and Br seps.  $\text{PhCHBrCHBrCO}_2\text{Et}$  and  $\text{CHNa}(\text{CO}_2\text{Et})_2$  gave as the main product *Et* phenylcyclopropanetricarboxylate, b<sub>p</sub> 108–11°. Hydrolysis of the ester gave carboxyphenylparaconic acid (VIII), prisms with 4  $\text{H}_2\text{O}$ , m. 83°, or anhyd., m. 187–8°; boiling with HCl gives phenylparaconic acid, m. 99–100°.  $\text{PhCBr}(\text{CBrCO}_2\text{Et})_2$  and  $\text{CHNa}(\text{CO}_2\text{Et})_2$ , condensed with 1 mol. EtONa, give an acid,  $\text{C}_{11}\text{H}_9\text{O}_4$ , m. 171–2°, probably contg. a lactone ring. Boiling with HCl gives phenylparaconic acid. In the absence of EtOH there results the ester  $\text{EtO}_2\text{CCH}(\text{CPhCBr}(\text{CO}_2\text{Et})_2)_2$ , b<sub>p</sub> 201–5°;

it reduces  $\text{KMnO}_4$  but does not react with  $\text{Br}$  in  $\text{CHCl}_3$ . The ester is unchanged by the action of  $\text{Na}$  in  $\text{C}_6\text{H}_6$  or  $\text{PhMe}$ ; hydrolysis with 60%  $\text{KOH}$  gives VIII. C. J. WEST

**Chlorination of 1-methylcyclohexan-4-one.** M. GODCHOT AND P. BEDOS. *Compt rend* 180, 295-7 (1925), cf. *C A* 18, 1990.—Direct chlorination of 1-methylcyclohexan-4-one gives only a poor yield of 3-chloro-1-methylcyclohexan-4-one (cf. Kötze and Steinhorst, *C A* 5, 1407), together with considerable proportions of poly Cl compds; the highly stable *dichloro-1-methylcyclohexan-4-one*,  $\text{C}_7\text{H}_{12}\text{OCl}_2$ , m 98-99°, was isolated. Chlorination by means of monochlorocarbamide (cf. Detouf, *C A* 16, 1395, 2113) yields 75% of 3-chloro-1-methylcyclohexan-4-one, which when divid. under diminished pressure, seps into 2 isomerides, probably of *cis-cis*- and *cis-trans*-configurations: (1) b 80-2°,  $d_4^{20}$  1.0994,  $n_D^{20}$  1.4705, and (2) b 112-10-12°,  $d_4^{20}$  1.0749,  $n_D^{20}$  1.4649. At the ordinary temp., each isomeride gradually undergoes partial transformation into the other, the form with the higher b p always predominating in the final mixt. This isomerization doubtless takes place with intermediate formation of the enolic compd., the ease with which the latter arises being due to the presence in the mol. of a Cl atom in the  $\alpha$ -position to the C=O group. Chlorocyclohexanone also forms an enolic modification spontaneously. B. C. A.

**The reaction between  $\alpha,\alpha'$ -dibromocyclohexanones and alkali.** GUDZO CUSMANO. *Gazz chim ital*, 55, 215-8 (1925).—In examples of these reactions between  $\alpha,\alpha'$ -dibromocyclohexanones (I) and alkali studied by C. (*C A* 8, 1760, 3021) and by Wallach (*C A* 13, 427) the final products are dihydropyrocatechols (II), which act as diketones or unsatd ketols. In repeating some work of W. (l. c.) C. has obtained the ketoglycol (III) which then gives methyldiketohexamethylene (IV) and (V). Thus I gives first the products of direct substitution, the  $\alpha,\alpha'$ -dihydroxyketones, and these by the loss



(III)



(IV)



(V)

of  $\text{H}_2\text{O}$  and internal oxidation and reduction form II. In the remainder of the paper C. discusses the mechanism of the loss of  $\text{H}_2\text{O}$  especially in connection with his own earlier work and that of W. and Wessenborn (reference not given). E. J. WITZEMANN

**Hydroaromatic 1,2-oxides and 1,2-oxide 3-ketones.** A. KÖTZ AND W. HOFFMANN. *J prakt Chem*, 110, 101-22 (1925).—Methyl- $\Delta^1$ -cyclohexene oxide (I) is catalytically reduced to 2'-hydroxy-1'-methylcyclohexanol. Methyl- $\Delta^1$ -cyclohexene oxide (II), b 143-4°, d 0.930. Catalytic reduction gives a mixt. of 3'- and 2'-hydroxy-1'-methylcyclohexanols. Catalytic reduction of methyl- $\Delta^1$ -cyclohexene oxide (III) gives a mixt. of 4'- and 3'-hydroxy-1'-methylcyclohexanols. Reduction of 1,2,3,4-tetrahydronaphthalene 1,2-oxide (IV) gives  $\beta$ -tetrahydronaphthol. III and  $\text{HCl}$  give principally 1-methyl-4-chlorocyclohexan-3-ol but there also results a small amt. of 1-methyl-3-chlorocyclohexan-4-ol. Cyclohexene oxide (V) and  $\text{EtOH}$  at 150° give 2-hydroxyethylcyclohexan-1-ol, b<sub>15</sub> 85-7°, oxidation with  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{H}_2\text{SO}_4$  gives 2-hydroxyethylcyclohexan-1-one, m 137-8°.  $\text{EtOH}$  and III gives an *Et ether* of 1-methylcyclohexan-2,4-diol, b<sub>15</sub> 90-3°, d<sub>15</sub> 0.946. V and  $\text{CHNa}(\text{CO}_2\text{Et})_2$  give the lactone of *Et 1-methylcyclohexan-1-ol-3-malonate*, b<sub>15</sub> 175-90°, d<sub>15</sub> 1.0735. III gives the lactone of *Et 1-methylcyclohexan-3-ol-4-malonate*, b<sub>15</sub> 183-5°, d<sub>15</sub> 1.0853, this was characterized by the formation of the diamide, m. 225-6°,  $\text{EtOH-KOH}$  gives a K salt, from which the free acid was obtained and heated to 90°, giving the lactone of 1-methylcyclohexan-3-ol-4-acetic acid, b<sub>15</sub> 143-9°, which was further oxidized to the known methylcyclohexan-3-one-4-acetic acid. V and  $\text{AcCHNaCO}_2\text{Et}$  give principally dehydroacetic acid, but a small amt. of the lactone of cyclohexan-1-ol-2-acetoacetic acid, b<sub>15</sub> 142-7°, mol wt. in freezing  $\text{C}_6\text{H}_8$ , 175. IV and  $\text{CHNa}(\text{CO}_2\text{Et})_2$  give products which may contain  $\alpha$ - and  $\beta$ -tetralone,  $\Delta^1$ - $\beta$ -Menthonone 3-oxide, b<sub>15</sub> 138-45°, d<sub>15</sub> 0.9992, with  $\text{CHNa}(\text{CO}_2\text{Et})_2$  this gives the lactone of an *Et 1-methyl-4-isopropylcyclohexanomalonalate*, b<sub>15</sub> 164-6°, d<sub>15</sub> 1.085.  $\text{CHNa}(\text{CO}_2\text{Et})_2$  and benzalacetone oxide give a lactone ester, b<sub>15</sub> 140-50°. C. J. WEST

**General method of synthesis of  $\omega$ -chloroallylated cyclic derivatives and of acetylenic hydrocarbons, alcohols, and cyclic aldehydes.** L. BERT. *Compt rend*, 180, 1504-6 (1925).—In toluene at 100°, the following reaction occurs  $\text{RMgX} + \text{CH}_2=\text{CH}-\text{CHCl}(\text{I}) = \text{RCH}=\text{CH}.\text{CHCl}(\text{II}) + \text{MgXCl}$ . II gives an aldehyde upon sapon., by the isomerization of the alc first formed. From  $\text{PhMgBr}$  and I is obtained nearly quant., a comjd.  $\text{C}_{11}\text{H}_{11}\text{Cl}$ , b 97°, b 212-4° (caled),  $d_4^{20}$  1.073,  $n_D^{20}$  1.545, which gives a dibromide, pale yellow oil with  $\text{CHCl}_3$  odor, b<sub>15</sub> 160°, d<sub>15</sub> 1.727,  $n_D^{20}$  1.611.  $\text{C}_8\text{H}_7\text{Cl}$  was identified as  $\omega$ -chloroallylbenzene, not  $\text{PhCH}=\text{CHCH}_2\text{Cl}$ , by its odor, phys consts.,

its dibromide, and chem. reactions. It resists sapon., but gives, with solid KOH and abs. alc at 130–5°, a liquid,  $C_{11}H_{11}O$ , of sweet, balsam odor,  $b_p$  127–8°,  $d_4^{15}$  0.970,  $n_D^{15}$  1.547, identified by its oxidation products as  $PhCH_2CH_2CHO$ . From  $RMgX$  and  $I$ , were obtained the following  $\omega$ -chloroalkylbenzene derivs: *o*-Me (III),  $b_p$  109°,  $d_4^{15}$  1.061,  $n_D^{15}$  1.545; *p*-Me (IV),  $b_p$  112.5°,  $d_4^{15}$  1.053,  $n_D^{15}$  1.542; *p*-Br (V),  $b_p$  140°,  $d_4^{15}$  1.433,  $n_D^{15}$  1.580, *p*-MeO (VI),  $b_p$  120°,  $d_4^{15}$  1.155,  $n_D^{15}$  1.553; *p*-iso-Pr (VII),  $b_p$  146°,  $d_4^{15}$  1.019,  $n_D^{15}$  1.532.  $\omega$ -Chlorobutenyl-*p*-isopropylbenzene (VIII),  $b_p$  148°,  $d_4^{15}$  1.015,  $n_D^{15}$  1.537; 2- $\omega$ -Chloroalkyl-*p*-cymene (IX),  $b_p$  140°,  $d_4^{15}$  1.018,  $n_D^{15}$  1.530. Di-bromides of the foregoing: III,  $b_p$  176.5°,  $d_4^{15}$  1.705,  $n_D^{15}$  1.599, IV,  $b_p$  174°,  $d_4^{15}$  1.695,  $n_D^{15}$  1.598; V,  $b_p$  204°,  $d_4^{15}$  1.975,  $n_D^{15}$  1.626; VII,  $b_p$  186–7°,  $d_4^{15}$  1.580,  $n_D^{15}$  1.587, IX,  $b_p$  196°,  $d_4^{15}$  1.531,  $n_D^{15}$  1.578. III, IV, etc give substituted cinnamyl alkyl ethers, which give substituted cinnamic acs., and these give the corresponding aldehydes. The substituted cinnamyl alkyl ethers give, on hydrogenation, substituted phenylpropyl alkyl ethers, yielding substituted phenylpropyl acs., and these yield the corresponding hydrocinnamic aldehydes. III, IV, etc, give acetylenic hydrocarbons on treatment with  $NaNH_2$ . In the fatty series, the yields are low. M. W. MCP.

The bromine addition products of the Schiff bases. M. A. BERG, *Bull. soc. chim.*, 37, 637–41 (1925).—The fixation of Br upon  $PhCH=NPh$  was studied by Hantzsch in 1890 (*Ber.* 23, 2714). On adding a soln. of Br to one of the base there is pptd. a pale yellow powder,  $PhCHBrNBrPh$ , m. 142° (decompn.). On contact with water it undergoes immediate decompn. to  $BzH$  and  $p$ - $BrC_6H_4NH_2$ ,  $HBr$ . In contact with anhyd. solvents the color of the powder persists and a metal, as Cu or Au, if introduced, is converted into a bromide. With solvents contg. water, the powder is decolorized—decompn. takes place as above and the metal is not attacked. Br addn. products upon other Schiff bases, differing in the nature of the radicals of the aldehyde and of the base, are often very sensitive to moisture and do not always give very consistent results for the detn. of Br. *Isobutylideneaniline* in anhyd.  $Et_2O$  added to Br in  $C_6H_6$  or  $CS_2$  gives a yellow powder evolving in moist air an irritating odor of  $Me_2CBrCHO$ , not altered by reducing agents and does not set free Br with  $HBr$ . On contact with water, the principal reaction is decompn. into  $Me_2CBrCHO + PhNH_2$ ,  $HBr$ . *Benzylideneisobutylamine*.—The Br addn. product, obtained as before, gradually forms a red-orange lower layer, slowly and incompletely forming ruby-red crystals, sepg. from  $CHCl_3$ , anhyd.  $Et_2O$  as a yellow cryst. powder, m. 83–4° (decompn.), has an irritating odor in moist air. With water, it decomps. into  $BzH + HBr + NHBrC_6H_5$ , *Isobutylideneisobutylamine*. Under the usual conditions there is obtained a thick red-orange liquid, which is very unstable. With water it decomps. into  $Me_2CBrCHO + C_6H_5NH_2$ ,  $HBr$ . *Benzylidenebenzylamine*.—The usual procedure gives in this case red crystals, m. 141–2°, slowly sol. in cold water with an irritating odor, becoming viscous on heating and giving off Br:  $PhCHBrNBrCH_2Ph + H_2O \rightarrow HBr + BzH + NHBrCH_2Ph$ ;  $NHBrCH_2Ph + HBr \rightarrow Br_2 + NH_2CH_2Ph$ . In conclusion, the decompn. of these Br derivs. by water is different according to the nature of the base and aldehyde that have produced the Schiff base. (1) One atom of Br passes into the amine nucleus when this is phenolic. The other yields  $HBr$  and the aldehyde is set free. (2) A brominated aldehyde is formed and a  $HBr$  salt of the base. (3) Br, being able to pass neither into the aldehyde group nor into the amine group, remains with the N in the form of a bromoamine. The other atom of Br yields  $HBr$  and the aldehyde is set free. H. W. G.

Iodine as a catalyst in reactions involving elimination of hydrogen halides. R. D. DESAI, *J. Indian Inst. Sci.* 7, 235–51 (1924).—On heating  $PhNH_2$  with 0.5 mol.  $PhCH_2Cl$  (I) for 10 min. at 50°, the use of 1% I (based on the  $PhNH_2$ ) increases the normal yield of  $PhNHCH_2Ph$  from 27 to 49%. If twice the amt. of I be used and the mixt. heated 6 hrs. at 97°, the yield of  $PhN(CH_2Ph)_2$  is 11%, if 1% I be added it is 47%, while if 1% I and 90%  $AcONa$  (both by wt. of the  $PhNH_2$ ) are added it is 98%. On heating equimol. amts. of  $PhNH_2$  and I for 10 hrs. at 105–10° with 0.5% I and 50%  $AcONa$  (by wt. of the  $PhNH_2$ ), the yield of  $PhNCH_2Ph$  (II) is 94%; it m. 88–85°. Its  $HCl$  salt and chloroplatinate having no definite m. p. Nitration of II in glacial  $AcOH$  by fuming  $HNO_3$  gives  $p$ - $O_2NC_6H_4NPhCH_2Ph$  (III), m. 163°; the amino compd. m. 100–1°, its  $Ac$  deriv. m. 201°, the  $Bz$  deriv. m. 245–6°. That the  $NO_2$  is not on the  $PhCH_2$  group is shown by the condensation of  $p$ - $O_2NC_6H_4CH_2Cl$  with  $PhNH_2$  to form 70% of  $p$ - $O_2NC_6H_4CH_2NPh$  (IV), m. 93.5°; the amino compd. is an oil whose  $Ac$  deriv. m. 165–6°, the  $Bz$  deriv. m. 136–7°; III and IV are thus sharply distinguished from each other. Heating II with 2.5 mols. S at 220° for 8 hrs. gives 25% of *benzylthiodi*.

phenylamine m 90.5–1°, the sulfone, by  $\text{KMnO}_4$  in  $\text{Me}_2\text{CO}$  contg.  $\text{AcOH}$ , m. 211–2°. If equimol amts of  $\text{CCl}_4$  and  $\text{Ph}_2\text{NH}$  are heated at 97–105° for several hrs. no trace of color develops but addn. of 0.2% I yields 9% of triphenylpararosaniline. In the reaction of the dialkylanilines with I the addn. of I catalyzes elimination of R (alkyl) Cl. Heating  $\text{PhNEt}_2$  with 0.5 mol I and 1% I at 150° for 20 hrs. gave approx. 40% of  $\text{PhCH}_2\text{NMePh}$  (V). Similarly I reacts with  $\text{PhNMe}_2$  (+I) to give  $\text{PhCH}_2\text{NMePh}$  (V), this also being formed by condensation of I with  $\text{PhNHMe}$  (+I), V b; 161–2°,  $d_{25}^{25} 1.0422$ ,  $n_D^{25} 1.6008$ , picrate m 128–8.5°.

WM. B. PLUMMER

Preparation and reactions of oximinooacetanilides. P. KARRER, G. H. DIECHMANN AND W. T. HAEBLER. *Helv. Chim. Acta* 7, 1631–9 (1924); cf. C. A. 18, 2144—*p*-Oximinooacetaminophenyl allyl ether, m. 177–8°, is obtained by Sandmeyer's method from *p*-aminophenyl allyl ether, and by electrolytic reduction is converted into glycine-*p*-allyloxylanilide, m. 98–9°. Similarly, 4-aminopyridine yields the corresponding oximinooacetyl deriv., m. 190–4°, and this is reduced to 4-glycylaminopyridine, an amorphous substance giving oily salts, only the picrolonate, m. 225–6°, being obtained crystalline. The oximinooacetyl deriv. of arsenic acid is likewise readily obtained, and also, from 3,4-H<sub>2</sub>N(HO)C<sub>6</sub>H<sub>3</sub>AsO<sub>3</sub>H<sub>2</sub>, 3-oximinooacetamino-4-hydroxybenzenearsonic acid, which is reduced by  $\text{SnCl}_2$  in the presence of a trace of KI to 3,3'-diglycylamino-4,4'-dihydroxyarsenobenzene, the HCl salt of which is described. When oximinooacetanilide is treated with warm  $\text{SOCl}_2$ , cyanoforamlanilide is readily produced, Oximinooacetylthranilic acid, similarly treated, affords cyanoforamlanthranil, m. 123°. This compd. is hydrolyzed when it is boiled with very dil. alc., and isic acid is produced; more complete hydrolysis, which takes place when the boiling is prolonged, produces anthranilic acid. Oximinooacetanilide is converted, by treatment with Cl in alc. HCl, into Dimroth and Taub's oxanilhydroxamic chloride (C. A. 1, 432). From the corresponding amino compds. the following derivs. were prepd.: *p*-oximinooacetaminooazobenzene, brown leaflets, m. 214°; *p*-toluene-3-azo-oximinooaceto-*p*-toluidide, m. 194°, and *p*-toluene-3-azo-oximinooaceto-*o*-toluidide.

B. C. A.

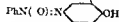
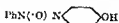
Addition compounds of 3,5-dibromo-*o*-toluidine with metallic salts. R. M. HANN AND G. C. SPENCER. *J. Wash. Acad. Sci.* 15, 163–5 (1925)—3,5,2-Br<sub>3</sub>(H<sub>2</sub>N)C<sub>6</sub>H<sub>3</sub>Me (B) heated with the various salts in alc., gave the following double salts: 2B HgCl<sub>2</sub>, m. ca. 120°; 2B ZnCl<sub>2</sub>, m. 211°; 2B CdBr<sub>2</sub>, not m. 225°; 2B CdCl<sub>2</sub>, not m. 200°. The complex-forming power of these metals did not interfere with the detn. of N as NH<sub>2</sub> by the "official" method.

B. H. NICOLET

Preparation of aryl isothiocyanates. I. Preparation of the tolyl isothiocyanates from *s*-di-*o*-tolylthiocarbamides. R. F. HUNTER. *Chem. News* 130, 370–2 (1925).—*s*-Di-*o*-tolylthiocarbamide, m. 161°, results in 30–40 g. yield from 50 g. *o*-MeC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>, 70 cc. EtOH, 80 cc. CS<sub>2</sub>, and 10 g. KOH; 32 g. of this, with 30 cc. Ac<sub>2</sub>O, gives 13–4 g. of *o*-MeC<sub>6</sub>H<sub>4</sub>NCS, b. 238–40°. Similar reactions were carried out with the *m*- and *p*-derivs.

C. J. WEST

Oxidation of benzeneazophenol. DINO BIGIARI AND GIORGIO KINDT. *Gazz. chim. ital.* 55, 83–6 (1925).—*p*-Hydroxyazobenzene with AcO<sub>2</sub>H gives a mixt. of *o*- and *p*-benzeneazoxyphenols (I) and (II), m. 156° and 117°, resp. A compd. (III), m. 240°, is also formed, this has now been studied. Eighty g. benzeneazophenol in 400 cc. AcOH was treated with 80 g. 30% H<sub>2</sub>O<sub>2</sub> and heated at 70–80° for 4 days. The



(V)

ppt. formed was filtered off; I was extd. with C<sub>6</sub>H<sub>6</sub> leaving 8 g. (C<sub>12</sub>H<sub>9</sub>O<sub>2</sub>N<sub>2</sub>)<sub>2</sub> (III), orange-yellow, m. 240°. Small amts. of III were obtained by oxidizing I with 30% H<sub>2</sub>O<sub>2</sub> in AcOH, or even with H<sub>2</sub>CrO<sub>4</sub>, PbO<sub>2</sub>, FeCl<sub>3</sub> in AcOH. With  $\text{SnCl}_2$  + HCl III is reduced after boiling roany hrs. to PhNH<sub>2</sub> and an oxidizable base, (C<sub>6</sub>H<sub>5</sub>ON)<sub>2</sub>, that decomps. without melting and was not identified. III boiled with excess Ac<sub>2</sub>O gave the *Ac* deriv. (IV), yellowish, m. 140–50°, mol wt. 550 (calcd. 510). IV reduced with Al Hg in Et<sub>2</sub>O gave a red product, m. 230°, that is not identical with azodiphenol, m. 184° (Robertson, Brady, C. A. 7, 3751). The Na salt of III boiled 4 hrs. with EtOH gave the *Et* ether, (C<sub>12</sub>H<sub>9</sub>O<sub>2</sub>N<sub>2</sub>)<sub>2</sub>, yellow-green, m. 218–22°. The formula V conforms with the analysis of III but does not conform with the data given above and with the fact that III is not formed from II.

E. J. WITZEMANN

Action of halogens on phenylhydrazones. II. The action of chlorine. J. E. HUMPHRIES, HENRY HICKLE AND ROY EVANS. *J. Chem. Soc.* 127, 1304–7 (1925); cf. C. A. 17, 3170—While Br enters the Ph nucleus atom by atom, chlorination leads directly to the di Cl deriv., even when a large excess of the phenylhydrazone is present. The reaction was effected by mixing 1 mol. of the components in CCl<sub>4</sub> at –5° to –10°.

$\text{Me}_3\text{C}:\text{NNHPh}$  gave the  $\text{HCl}$  salt of the mono- $\text{Cl}$  deriv. *Acetophenone 2,4-dichlorophenylhydrazone*, yellow, m.  $85^\circ$ ; *benzophenone deriv.*, yellow, m.  $105^\circ$ ; further substitution gave the 2,4,6-tri- $\text{Cl}$  deriv., m.  $106^\circ$ .  $\text{PhCH}:\text{NNHPh}$  and 1 mol  $\text{Cl}$  gave a mixt. of  $\text{Cl}$  derivs. which could not be sep'd, the  $p$   $\text{Cl}$  deriv. gave the tri- $\text{Cl}$  deriv.,  $\text{PhCCl}:\text{NNHC}_6\text{H}_4\text{Cl}_2(2,4)$ , m.  $90^\circ$ , the 2,4  $\text{Cl}$  deriv. gave the same deriv. Reduction in boiling  $\text{EtOH}$  with  $\text{Zn}$  dust gives 2,4- $\text{Cl}_2\text{C}_6\text{H}_3\text{NHNH}_2$   $\text{HCl}$  *m* *Chlorobenzaldehyde 2,4-dichlorophenylhydrazone*, yellow, m.  $127^\circ$ ;  $p$ -deriv., m.  $117^\circ$ .  $\text{PhCCl}:\text{NNHC}_6\text{H}_4\text{Cl}$  gives a tetra- $\text{Cl}$  deriv., yellow, m.  $98^\circ$ , mol wt in freezing  $\text{C}_6\text{H}_6$  347, which is reduced by  $\text{Zn}$  dust in boiling  $\text{EtOH}$  to 2,4,6- $\text{Cl}_3\text{C}_6\text{H}_2\text{NHNH}_2$   $\text{HCl}$  and furnishes probably the best method for its prep'n  $p$  *Bromobenzaldehyde 2,4-dibromophenylhydrazone*, orange-yellow, m.  $128^\circ$ . C. J. WEST

**Colloidal organomercuric compounds.** G. ROSSI AND C. BOCCHI. *Gazz. chim. ital.* 55, 93-6(1925).—In previous papers Raffo and Rossi (*C. A.* 7, 1724, 8, 2775; 16, 2489) described penta-, tetra-, and trimercuroacetanilide, which all give aq. colloidal solns, while the mono- and di derivs. obtained by Pesci do not give colloidal solns. in  $\text{H}_2\text{O}$ . R. and B. synthesized another series of these compds. to see if they also show this transition in properties. 1.49 g  $o$ -acetotoluide (I) + 12.72 g  $\text{Hg}(\text{OAc})_2$  were heated gradually from  $100^\circ$  to  $166^\circ$  and gave a gelatinous product, *tetramercuro- $o$ -acetotoluide acetate* that was slowly completely sol in  $\text{H}_2\text{O}$ . This yellowish soln is viscous, coagulates at  $100^\circ$  but the coagulum redissolves on cooling. 1.49 g I + 9.54 g  $\text{Hg}(\text{OAc})_2$  treated similarly gave *trimercuro- $o$ -acetotoluide acetate* as a transparent glass that was slowly sol in  $\text{H}_2\text{O}$ . The solns of these compds treated with dil solns of  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{NaOH}$ ,  $\text{KOH}$ , alkali and alk. earth salts give abundant ppts due in part to true coagulation. The corresponding dimercure compound prep'd by Schoeller (*C. A.* 7, 481) does not appear to give colloidal solns. E. J. WITZEMANN

**$p$ -Arsonobenzeneazophthalains.** W. G. CHRISTIANSEN. *J. Am. Chem. Soc.* 47, 2244-9(1925).—When a soln. of  $p$ - $\text{H}_2\text{O}_2\text{AsC}_6\text{H}_4\text{N}_2\text{Cl}$  is added to an alk. soln. of an equiv. quantity of a phthalain, coupling takes place, the product can be fractionated by pptn. from aq. alk. soln. with  $\text{EtOH}$  into unchanged phthalain, and its mono- and diarsonobenzeneazo derivs. Phenolphthalain (7.3 g) gave 4 g. of  $o$ -4-arsonobenzeneazophenolphthalain, orange (total dose, det'd. by intravenous injection of alk. soln. into albino rats, <100 mg./kg.; this value given in ( ) for other compds.) and 0.8 g. of the  $o,o'$ -di-4-arsonobenzeneazo deriv., dark brown (180), and 3.2 g. of a mixt. of about equal amts. of the 2 derivs. Phenoltetrachlorophthalain (3 g.) gave 0.8 g. of the  $o$ -4-arsonobenzeneazo deriv., brown-orange (<300) and 1 g. of the  $o,o'$ -di-4-arsonobenzeneazo deriv., dark brown (<500). Fluorescein (6.5 g) gave 3.1 g. of the  $o$ -4-arsonobenzeneazo deriv., dark orange (>200) and 3.5 g. of the  $o,o'$ -di-4-arsonobenzeneazo deriv., brick-red (>280). Dibromofluorescein (8.1 g.) gave 3.5 g. of the  $o$ -4-arsonobenzeneazo deriv., red-orange (>1000) and 0.4 g. of the  $o,o'$ -di-4-arsonobenzeneazo deriv., deep red. Phenolsulfonephthalain gave a dark red powder which was not fractionated, it is tolerated in doses above 1.8 g./kg. None of these compds is trypanocidally active. The color in 0.04  $N$   $\text{NaOH}$  and in concd.  $\text{H}_2\text{SO}_4$  is given and the fluorescence noted. The rate of excretion is discussed. C. J. WEST

**Directing influence of the methanesulfonyl group.** R. F. TWIST AND SAMUEL SMILES. *J. Chem. Soc.* 127, 1248-52(1925).—Bourgeois and Abraham (*C. A.* 6, 623) assign a  $p$ -directive influence to the  $\text{SO}_2\text{Me}$  group; since the  $\text{SO}_2\text{H}$  and  $\text{SO}_2\text{Ph}$  groups give  $m$ -derivs., the work has been reinvestigated and only  $m$ -derivs. have been found. 3-Nitrophenyl methyl sulfone, m.  $146^\circ$ , by nitration of  $\text{PhSO}_2\text{Me}$  or from  $\text{MeI}$  and  $m\text{-O}_2\text{NC}_6\text{H}_4\text{H}_2\text{SO}_4\text{Ag}$ ; further by heating  $m\text{-O}_2\text{NC}_6\text{H}_4\text{SO}_2\text{CH}_2\text{CO}_2\text{H}$ , m.  $62^\circ$ , which results upon nitrating  $\text{PhSO}_2\text{CH}_2\text{CO}_2\text{H}$ .  $m\text{-C}_6\text{H}_4(\text{SO}_2\text{Me})_2$  was prep'd. from the  $\text{Ag}$  salt and  $\text{MeI}$  and also as follows:  $\text{PhSO}_2\text{Me}$  and  $\text{ClSO}_2\text{H}$  give  $m$ -chlorosulfonylphenyl methyl sulfone, m.  $94^\circ$ , which is reduced by  $\text{Sn}$  and  $\text{HCl}$  to the mercaptan, m.  $69^\circ$  (also obtained from a soln. of  $\text{MeO}_2\text{SC}_6\text{H}_4\text{SO}_2\text{H}$ , which is converted by  $\text{HI}$  into phenyl methyl sulfone  $m$ -disulfide, m.  $200^\circ$ , which, in turn, gives with aq.  $\text{NaOH}$  the  $m$ -disulfide, pale yellow, m.  $120^\circ$ , which is further hydrolyzed to the mercaptide and converted into the mercaptan); with  $\text{Me}_2\text{SO}$  this yields  $m$ -methylthiophenyl  $\text{Me}$  sulfone, m.  $53^\circ$ , which is oxidized by  $\text{H}_2\text{O}_2$  in glacial  $\text{AcOH}$  to  $m\text{-C}_6\text{H}_4(\text{SO}_2\text{Me})_2$ . 3-Bromophenyl  $\text{Me}$  sulfone, m.  $103^\circ$ , results by brominating  $\text{PhSO}_2\text{Me}$  or from 3- $\text{BrC}_6\text{H}_4\text{SO}_2\text{H}$ ; the 4- $\text{Br}$  deriv. also m.  $103^\circ$ , but a mixt.  $m$ . indefinitely at  $70^\circ$ . C. J. WEST

**Alkylation with esters of  $p$ -toluenesulfonic acid.** C. FINZI. *Ann. chim. applicata* 15, 41-50(1925).—Esters of  $p\text{-MeC}_6\text{H}_4\text{SO}_3\text{H}$  were found to be a very effective means of introducing alkyl groups in phenols, aromatic amines and aromatic acids. This could not be carried out in  $\text{EtOH}$ , because of decompn. of the ester; the most satisfactory solvent with phenols was  $\text{H}_2\text{O}$ , with acids was alk. solns, while with amines no solvent

was necessary. Most phenols and amines reacted easily and only a short boiling of equimol wts of the Na phenate and ester was required. The good yield reported by Ulmann and Werner in the prepn. of  $p\text{-MeC}_6\text{H}_4\text{SO}_3\text{Et}$  (*Ann.* 327, 120) could not be obtained by their procedure. Instead equal wts. of 95-6% EtOH and crude  $p\text{-MeC}_6\text{H}_4\text{SO}_3\text{Cl}$  were mixed and let stand at  $30^\circ$  until odorless (usually 6-7 days), then poured into 3-4 vols of  $\text{H}_2\text{O}$ , decanted, the heavy oil ( $p\text{-MeC}_6\text{H}_4\text{SO}_3\text{Et}$ ) filtered and cooled to  $5\text{-}10^\circ$  until all had crystd., m  $34^\circ$ . The following compds. were prepd with the aid of crude  $p\text{-MeC}_6\text{H}_4\text{SO}_3\text{Me}$  or of  $p\text{-MeC}_6\text{H}_4\text{SO}_3\text{Et}$ . *PhOEt*. Equimol. wts of  $\text{PhOH}$  and  $\text{NaOH}$  (10% soln) boiled with a slight excess of  $p\text{-MeC}_6\text{H}_4\text{SO}_3\text{Et}$  gave a cryst mass which on addn of  $\text{H}_2\text{O}$  sepd. into 2 layers. By extn with  $\text{Et}_2\text{O}$ , drying with  $\text{CaCl}_2$ , evapn and fractionation the yield was 80%.  $\text{MeC}_6\text{H}_4\text{OEt}$ . By the same procedure the yield was 85%  $m\text{-C}_6\text{H}_4(\text{OEt})_2$ . Resorcinol (5.5 g) and 10%  $\text{NaOH}$  (40 cc) boiled with  $p\text{-MeC}_6\text{H}_4\text{SO}_3\text{Et}$  (22 g.) and treated like the preceding compds. gave an 82% yield  $p\text{-C}_6\text{H}_4(\text{OEt})_2$ . The same procedure gave an 84% yield.  $o\text{-MeOC}_6\text{H}_4\text{OEt}$ . The same procedure gave an 80% yield. *Na p-bisazostilbenepheneole-o-disulfonate* (chrysophenin). By boiling brilliant yellow,  $(\text{HOCH}_2\text{CH}_2\text{N}^+\text{NC}_6\text{H}_4(\text{SO}_3\text{Na})_2\text{CH}_2\text{CH}_2\text{OH})$  in  $\text{H}_2\text{O}$  with  $\text{NaOH}$  (2 mols) and  $p\text{-MeC}_6\text{H}_4\text{SO}_3\text{Et}$  (4 mols), chrysophenin sepd. in increasing amts as boiling proceeded. On cooling it was freed of admixed monoethylated brilliant yellow by washing with 5% aq  $\text{NaCl}$  contg. 3%  $\text{NaOH}$  and then with  $\text{H}_2\text{O}$ . The yield of chrysophenin was 68-70% and it had double the coloring power of the best com. grades and had only 0.25% ash (above the theoretical). The mother liquors yielded on standing 4% more. *PhNIEt*.  $\text{PhNH}_2$  and  $p\text{-MeC}_6\text{H}_4\text{SO}_3\text{Et}$  (slightly over 1 mol) heated at  $175\text{-}85^\circ$  for 1 hr., cooled, let cryst., treated with dil.  $\text{NaOH}$ , the 2 layers sepd., extd. and fractionated, gave a yield of 83%.  $o\text{-MeC}_6\text{H}_4\text{NIEt}$ . The same procedure as that for  $\text{PhNIEt}$  gave an 80% yield. *N-Ethyl-m-toluidine*, prepd like the preceding 2 compds from *m*-toluidine and  $p\text{-MeC}_6\text{H}_4\text{SO}_3\text{Et}$  (2 parts), oil, b  $215^\circ$ ; *Ac deris.* from  $m\text{-MeC}_6\text{H}_4\text{NH}_2$ ,  $\text{Ac}_2\text{O}$  and  $\text{NaOAc}$ , oil, b  $254^\circ$ .  $p\text{-MeC}_6\text{H}_4\text{NIEt}$  was prepd. like its isomers and in the same yield. *BzOEt*. Equimol. wts of  $\text{BzOH}$ ,  $\text{Na}_2\text{CO}_3$  (10% soln.) and  $p\text{-MeC}_6\text{H}_4\text{SO}_3\text{Et}$  were boiled 20 min., cooled, let cryst., treated with  $\text{H}_2\text{O}$  to form 2 layers, extd. with  $\text{Et}_2\text{O}$ , dried with  $\text{CaCl}_2$ , the  $\text{Et}_2\text{O}$  evapd. and the product fractionated.  $o\text{-HOC}_6\text{H}_4\text{CO}_2\text{Et}$ . The same procedure as for  $\text{BzOEt}$  gave a 75% yield.  $o\text{-HOC}_6\text{H}_4\text{CO}_2\text{Me}$ . The same procedure was followed, using  $p\text{-MeC}_6\text{H}_4\text{SO}_3\text{Me}$ .  $o\text{-EtHNC}_6\text{H}_4\text{CO}_2\text{H}$  was prepd. from  $o\text{-H}_2\text{NC}_6\text{H}_4\text{CO}_2\text{H}$  (13 g.), the corresponding amt. of 10%  $\text{NaOH}$  and  $p\text{-MeC}_6\text{H}_4\text{SO}_3\text{Et}$  (20 g.) by boiling 1 hr., cooling until crystd., adding  $\text{H}_2\text{O}$  to sep. the oil, washing the latter and crystg from  $\text{EtOH}$ .  $p\text{-MeHNC}_6\text{H}_4\text{CO}_2\text{H}$ . Following the procedure for  $o\text{-EtHNC}_6\text{H}_4\text{CO}_2\text{H}$  except for the use of  $p\text{-MeC}_6\text{H}_4\text{SO}_3\text{Me}$  and  $p\text{-H}_2\text{NC}_6\text{H}_4\text{CO}_2\text{Na}$ , the product m  $228^\circ$ , agreeing with the data of Hauben (*Ber.* 37, 3079(1904)) and not with those of other workers (cf. Jaffé, *Z. physiol. Chem.* 43, 374-66(1905)). High yields were also obtained in the alkylation of  $\alpha$ - and  $\beta$ -naphthol and  $o$ - and  $p$ - $\text{HOC}_6\text{H}_4\text{NO}_2$ , but  $\text{HOC}_6\text{H}_4(\text{NO}_2)_2$ ,  $\text{HOC}_6\text{H}_4(\text{NO}_2)_2$  and  $(\text{HO})_2\text{C}_6\text{H}_2(\text{NO}_2)_2$  did not react even after prolonged boiling with a large excess of alkylating ester, nor did alkylation of mononitroanilines proceed to any considerable degree.

C. C. DAVIS

Catalytic dehydration of phenol-alcohol systems. E. BRINER, W. FLETCHER and H. YALLARD. *Indr. Chim. Asto* 7, 1048-56(1924).—When a mixt. of phenol (or cresol, xylenol, resorcinol or pyrogallol) and  $\text{MeOH}$  is passed over alumina at  $400\text{-}440^\circ$  hexamethylbenzene is produced. When  $\beta$ -naphthol is similarly treated a new tetramethylnaphthalene, m  $104\text{-}5^\circ$ , is obtained.

H. C. A.

Molecular condition of phenol in benzene solution. J. C. PHILIP and C. H. D. CLARK. *J. Chem. Soc.* 127, 1274-7(1925); cf. P. and Bramley, *C. A.* 9, 1572; Rothmund and Walmore, *Z. physik. Chem.* 40, 611(1902).—The ratio [concn. in  $\text{H}_2\text{O}$  phase]/[concn. in  $\text{C}_6\text{H}_6$  phase] is practically constant at low  $\text{PhOH}$  concns., the departure from constancy occurring when the amt. of  $\text{PhOH}$  per l. of  $\text{C}_6\text{H}_6$  layer has risen to about 28 g. This confirms the work of P. and B. and of R. and W. The same change was observed for a  $\text{NaCl}$  soln and  $\text{C}_6\text{H}_6$  at about the same  $\text{PhOH}$  concn. These results indicate that in the lowest concn. range the  $\text{PhOH}$  in the  $\text{C}_6\text{H}_6$  soln has reached a steady mol condition, i.e., corresponding with simple  $\text{PhOH}$  mols. In the more concd solns. there are probably double and triple mols.

C. J. WEST

Reduction of anethole nitroschloride by stannous chloride and hydrochloric acid. J. B. SHOESMITH and K. H. SEATON. *J. Chem. Soc.* 127, 1490(1925).—Reduction of anethole nitroschloride (Orndorff and Morton, *Am. Chem. J.* 23, 191) in  $\text{CHCl}_3$  with  $\text{SnCl}_2$  and  $\text{HCl}$  gives anisylideneazane- $\text{HCl}$ , yellow, m  $172^\circ$ , decomp.  $177^\circ$ , which ppt. as the chloroannine, yellow, m  $259^\circ$ .

C. J. WEST

Laboratory method of preparing *p*-benzoquinone. REGINALD CRAVEN and W. A.

T. DUNCAN. *J. Chem. Soc.* 127, 1489(1925) —Quinol (66 g.) in 300 cc. 60% AcOH is treated with stirring with 200 cc 30% AcOH contg. 84 g.  $\text{CrO}_3$ , at a temp. below  $10^\circ$ . The yield of *p*-benzoquinone, m.  $114.5^\circ$ , is 30–40 g. C. J. WEST

Action of azides on toluquinone. F. D. CHATTAWAY AND G. D. PARKES. *J. Chem. Soc.* 127, 1307–11(1925), cf. Wolff, *C. A.* 7, 788, 3740 — $\text{PhN}_3$  and toluquinone (I) give phenylaziminotoluquinone, yellow, m.  $206^\circ$ , which loses N on prolonged heating with  $\text{C}_2\text{H}_6$  or a few min. with  $\text{PhNH}_2$ , giving phenylcycloiminotoluquinone, pale yellow, m.  $130^\circ$ . *o*- $\text{MeC}_6\text{H}_4\text{N}_3$  and I give *o*-tolylaziminotoluquinone, m.  $155^\circ$ , which was not obtained pure as it evolved N during recrystn. *o*-Tolylcycloiminotoluquinone, Au-yellow, m.  $139^\circ$ , sol. in  $\text{H}_2\text{SO}_4$  or EtOH-KOH with a dark crimson color, hydrolyzed by boiling aq. KOH to *o*- $\text{MeC}_6\text{H}_4\text{NH}_2$ , and does not react with  $\text{H}_2\text{NCONHNH}_2$ , boiling  $\text{PhOH}$ ,  $\text{PhNH}_2$ , NaOBr, Su and HCl,  $\text{HNO}_2$  or  $\text{Ac}_2\text{O}$ . The following derivs were also prepd.: *p*-chlorophenyl, yellow, m.  $180^\circ$ , 2,4-dichlorophenyl, yellow, m.  $209.5^\circ$ ; 2,6-dichlorophenyl, yellow, m.  $229^\circ$ ; *p*-bromophenyl, yellow, m.  $185^\circ$ ; 2,4-dibromophenyl, yellow, m.  $216^\circ$ ; 2,4,6-tribromophenyl, yellow, m.  $171^\circ$ . C. J. WEST

Dyes and other derivatives of cresorcinol. F. HENRICH AND F. GÖTZ. *Ber.* 58B, 1055–60(1925); cf. *C. A.* 17, 2111 —It had been found that when 5,2,4-Me(HO) $_3$ - $\text{C}_6\text{H}_3\text{NH}_2$ ·HCl (I) in concd soln is treated with the amt. of 1% NaOH or KOH necessary to form the mono-alkali salt, the soln eagerly absorbs O, becomes intensely bright blue and gradually deposits a substance (II) which after a time again disappears, especially if an excess of alkali is present;  $\text{NH}_3$  is evolved, the soln. becomes more violet, often with a stronger tinge of reddish, and shows strong fluorescence on diln., and acids ppt. a 2nd colored oxidation product (III). To obtain the intermediate product (II) the soln. of the mono-Na salt of I was allowed to stand in the ice chest until the II did not increase in amt. (about 2 hrs) and the II was freed of inorg. matter by washing with  $\text{H}_2\text{O}$ ; yield, 0.9 g from 3.4 g. I. II,  $\text{C}_{10}\text{H}_9\text{O}_4\text{N}$ , yellow, becomes faintly orange about  $100^\circ$ , more intensely orange  $130$ – $60^\circ$ , darkens about  $180^\circ$ , dissolves, when fresh, with pure blue color (without fluorescence) in alkalis and is turned red by acids; it was therefore assumed to be 3,3'-dimethyl-6,4',6'-trihydroxyindophenol. It dissolves easily in AcOH with reddish color but III soon seps, concd  $\text{H}_2\text{SO}_4$  dissolves it with bright blue color and reddish tinge and  $\text{H}_2\text{O}$  ppts. III; the blue soln. with greenish tinge in dil. NaOH gradually changes more and more to reddish with strong fluorescence and acids ppt. III; acetylation gives the Ac deriv of III. III, highly red, has the same compn as II and, from its fluorescence, is assumed to be a hydrate of 3,6-dimethyl-7-hydroxy-2,10-phenoxazone (IV), and as a matter of fact 0.1572 g. heated 1–2 hrs at  $150^\circ$  loses 0.0106 g.  $\text{H}_2\text{O}$  and changes to a red-brown substance having the compn.  $\text{C}_{14}\text{H}_{11}\text{O}_4\text{N}$ . III dissolves in  $\text{Na}_2\text{CO}_3$  with blue color but no fluorescence and diln. produces a Cu color and strong fluorescence; it is insol in dil acids and dissolves in cold concd acids with blue-red color, diln. reprecipitates it. Boiled with 10 parts  $\text{Ac}_2\text{O}$ , it gives a monoacetate, bright orange-yellow, m.  $216$ – $8^\circ$ , mol wt. in boiling  $\text{C}_2\text{H}_5$  263, sol in concd.  $\text{H}_2\text{SO}_4$  with blue-red color; with hot concd HCl it forms a dark substance which with  $\text{H}_2\text{O}$  regenerates III. With 2 mols. Br in AcOH III yields a di-Br deriv. (V),  $\text{C}_{12}\text{H}_7\text{O}_4\text{NBr}_2$ , dark crystals with cantharides luster, blackens above  $230^\circ$ , does not m.  $310^\circ$ , in NaOH with blue-red color and very faint fluorescence. Bromoaminocresorcinol-HBr, from I and 1 mol Br; in AcOH, Ag-gray, evolves Br copiously when heated with concd.  $\text{H}_2\text{SO}_4$  and  $\text{MnO}_2$ ; when it is treated in  $\text{H}_2\text{O}$  with the calcd. amt. of NaOH to form the mono-Na salt the soln. absorbs O and becomes deep blue at first and after a long time violet without any marked fluorescence. Acidification before the appearance of the violet color ppts a dibromoindophenol,  $\text{C}_{14}\text{H}_{11}\text{O}_4\text{NBr}_2$  (VI), crystals with cantharides luster, sol. in alkalis with pure blue color and no fluorescence and acting as a very sharp indicator, which in great diln. changes from deep blue to bright red; it dissolves in concd.  $\text{H}_2\text{SO}_4$  with blue color, changing to red, with pptn. of the VI, on diln.; with  $\text{H}_2\text{SO}_4$ - $\text{MnO}_2$  it gives considerably less Br than the parent compd.; triacetate, yellow-orange, slowly sol. in alkalis with deep blue color. Towards acids, VI is considerably more stable than II; only after long boiling with moderately concd. HCl does it yield V, which forms a red-brown acetate. 2,4,3,5-(HO) $_2$ (ON) $_2$ - $\text{C}_6\text{H}_2\text{Me}$  (v. Kostanecki, *Ber.* 20, 3135(1887)), yellow, darkens  $150^\circ$ , deflagrates  $169^\circ$ , is obtained in satisfactory yield from cresorcinol in 3 parts alc. with 2 mols  $\text{AmONO}$ ;  $\text{SnCl}_2$ ·HCl reduces it to diaminocresorcinol·2HCl, darkens about  $220^\circ$ , decomps.  $286$ – $8^\circ$ , whose aq. soln., made very faintly alk., undergoes autooxidation in the air, becoming blue at first and then gradually colorless; refluxed in 10 parts  $\text{Ac}_2\text{O}$  it yields tetraacetyldiaminocresorcinol,

m.  $134^\circ$ , which on dry distn. forms a compd.  $\text{MeC}_6\text{H}_2\left[\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{N} \end{array}\right]\text{CMe}$ , m.  $144^\circ$ .

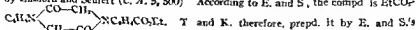
C. A. R.

Spectrophotometric determination of hydrogen-ion concentrations and of the apparent dissociation constants of indicators. IV. 1-Naphthol-2-sodium sulfonate-indophenol. W. C. HOLMES AND E. F. SVYDER. *J. Am. Chem. Soc.* 47, 2232-6 (1925); cf. C. A. 19, 772.—1-Naphthol-2-sodium sulfonate-indophenol is relatively unstable in aq. solns. but is stable in abs. EtOH. The dissociation of the dye follows the normal course of a monobasic acid. The apparent dissociation const. is 8.63 in aq. solns. contg. 5% of EtOH. Data are supplied for the application of the indicator in the detn. of H-ion exponents by the spectrophotometric and drop-ratio methods. C. J. WEST.

Isomerism of the oximes. XXII. The configuration of the aldoximes. O. L. BRABY AND GERALD BISHOP. *J. Chem. Soc.* 127, 1357-62 (1925); cf. C. A. 19, 2039.—A review of the recent work on aldoximes makes it appear doubtful whether Hantzsch's assumption that cis-elimination of AcOH takes place from the Ac derivs. of the aldoximes can be maintained and there are considerable grounds for suggesting that the configuration of all these compds. be reversed. For the present, however, the designations  $\alpha$  and  $\beta$  are used, the  $\alpha$ -oxime is that which on treatment with AcO at 30° gives an Ac deriv. which on hydrolysis regenerates the original oxime, while the  $\beta$ -oxime is that which under similar conditions gives the nitrile or corresponding acid.  $\alpha$  Acyl derivs. are those which on hydrolysis regenerate the oximes,  $\beta$  acyl derivs., those which give the nitrile or acid.  $\alpha$ -Acetyl-2-chloro-5-nitrobenzaloxime, pale buff, m. 110°; warmed with 2 N NaOH, the original oxime was obtained. The  $\alpha$ -oxime ground with HCl, cooled and satd. with HCl gives the  $\beta$ -2-chloro-5-nitrobenzaloxime, very pale yellow, m. 176°, the Ac deriv., on hydrolysis, gives the 2,5-Cl(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>H. The action of alkali on these two forms is discussed. C. J. WEST.

Benzoyl hydroperoxide: preparation and application to organic synthesis. HAROLD HIBBERT AND C. PAULINE BURT. *J. Am. Chem. Soc.* 47, 2240-3 (1925).—Bz<sub>2</sub>O<sub>2</sub> (121 g.) and 1.5 l. Et<sub>2</sub>O at -5° are treated with the calcd. amt. of approx. 10% EtONa over a period of 15 min., the temp. being maintained at -5°; after stirring for 15 min. further, 300 cc. ice H<sub>2</sub>O is added and the aq. layer contg. Na benzoylhydroperoxide is slowly dropped into a cooled soln. of 240 cc. 20% H<sub>2</sub>SO<sub>4</sub> at 0°; the free hydroperoxide is extd. with CHCl<sub>3</sub>, yield, 90%. Evapn. of a CHCl<sub>3</sub> soln. yields a paste contg. 20-30% of hydroperoxide, on further evapn. this decomps. into BrOH. A CHCl<sub>3</sub> soln. dried over Na<sub>2</sub>SO<sub>4</sub> at 0° may be kept exposed to light at room temp. for a no. of days without appreciable decompn. At about 320°, PhCH<sub>2</sub>CO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph decomps. into PhCH=CH<sub>2</sub> and PhCH<sub>2</sub>CO<sub>2</sub>H, the yield of PhCH=CH<sub>2</sub> being 60%. Styrole oxide is obtained in 75% yields from PhCH=CH<sub>2</sub> and benzoylhydroperoxide. C. J. WEST.

Condensation of *p*-aminobenzoic esters with chloroacetic acid. Z. TAKEEDA AND S. KURODA. *J. pharm. Soc. Japan*, No. 515, 22-38 (1925).—In order to obtain derivs. of anesthesine in which the NH<sub>2</sub> group is substituted with -CH<sub>2</sub>CO<sub>2</sub>H, the above condensation was attempted. When anesthesine and COCH<sub>2</sub>CO<sub>2</sub>H were mixed in equimol. ratio and heated on the water bath, 3 products were obtained. When the products were treated with HCl to remove the unchanged anesthesine and extd. with an alkali carbonate soln., there was isolated the desired Et phenylglycine-*p*-carboxylate (I), sol. in the alkali carbonate and insol. in HCl, m. 157-60°. The residue contains 2 substances, an alc.-sol. (II), and an alc.-insol. (III). The II, m. 110-1°, and is *p*-ClCH<sub>2</sub>CONHC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>Et. III, m. 215°, has the compn. C<sub>23</sub>H<sub>20</sub>O<sub>4</sub>N<sub>2</sub>, and that it is probably a condensation product of the intermediate product in this reaction with anesthesine is shown by the fact that treating II with anesthesine gives III. III, therefore, must be di-Et *p*-carboxyphenylglycylamino benzoate which has been previously prepd. by Emhorn and Seufert (C. A. 5, 500). According to E. and S., the compd. is EtCO-



method and found it to be identical with III. According to the formula given by E. and S. this compd. should not form a nitroso deriv. with HNO<sub>3</sub>. T. and K. found, however, both III and the compd. prepd. by E. and S.'s method give a nitroso deriv., C<sub>23</sub>H<sub>17</sub>O<sub>5</sub>N<sub>2</sub>, m. 145-9°. Thus III must have the structure EtOCC<sub>6</sub>H<sub>4</sub>NHCOCH<sub>2</sub>NHC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>Et. When III is saponified with alc. KOH, HO<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>NHCH<sub>2</sub>CONHC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H (IV) is obtained. If IV is further heated in 10% KOH in a sealed tube at 150° for 1 hr., or 3 hrs. under atm. pressure and treated with HCl, *p*-HO<sub>2</sub>CCH<sub>2</sub>NHC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H, m. 235°, is obtained. When I is saponified, IV can also be obtained easily. The results of the condensation of the Me, Pr, iso-Pr and benzyl esters of *p*- and *m*-H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H and ClCH<sub>2</sub>CO<sub>2</sub>H are given. S. T.

Synthesis of the *m*-dihydroxycinnamic acids. F. MAUTHNER. *J. prakt. Chem.* 110, 123-8, 1935.—*m*-(HO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CHO and CH<sub>2</sub>(CO<sub>2</sub>H)<sub>2</sub> in EtOH contg. a little piperidine

give 3,5-dihydroxycinnamic acid, m. 215-6°, *d*<sub>1</sub>-Me ether, m. 175-6°. *m*-(MeO)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>CHO, PhCONHCH<sub>2</sub>CO<sub>2</sub>H, AcONa and Ac<sub>2</sub>O give an *azlactone*, C<sub>16</sub>H<sub>11</sub>O<sub>2</sub>N, yellow, m. 156-7°, which is split by 10% NaOH and oxidized by H<sub>2</sub>O<sub>2</sub> to give 3,5-dimethoxyphenylacetic acid, m. 99-100°. 1,3-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>OH and chloral hydrate are condensed by K<sub>2</sub>CO<sub>3</sub> to form 2-hydroxy-1,3 dimethoxyphenyltrichloromethylcarbinol, m. 162-3°.

C. J. WEst

**Hydrogenation of the triple bond. Formation of *cis*-ethylene compounds.** M. BOURGUEL. *Compt. rend.* 180, 1753-5 (1925).—By carrying out the hydrogenation of compds. contg. a triple bond catalytically at low temps., *cis*-compds. were formed instead of the *trans*-isomers or the mixts. of *trans*- and *cis*-isomers obtained in all hydrogenation expts. in the past. Colloidal Pd adsorbed on starch in amts. of 0.01-0.03 g. per 15-30 g. of unsatd. compd. served as catalyst. With PhC CCO<sub>2</sub>H the results of Paal and Hartmann (no reference) were confirmed, no *trans*-cinnamic acid being found. PhC:CPh (17 g.) gave almost solely isostilbene (14.5 g.) with a residual mixt. (0.4 g.) of dibenzyl and stilbene. (HO<sub>2</sub>CC)<sub>2</sub> (in H<sub>2</sub>O or EtOAc) gave only malic acid. Tetrollic acid (26 g.) gave only isocrotic acid (23 g.). Tetramethylbutinediol (60 g.) gave almost wholly the *cis*-compd. m. 67-8°, but after successive crystns. was obtained a little of the *trans*-isomer (0.3 g.), m. 76.5°, probably the compds. obtained by Salkind (no reference) which m. 69.5° and 76.5°, resp.

C. C. DAVIS

**Conversion of gallic acid trimethyl ether into gallic aldehyde trimethyl ether.** ADOLF SONN and WALTER MEYER. *Ber* 58B, 1096-103 (1925); cf. C. A. 14, 1985.—The reaction whereby BzOH can be converted quant. into BzH (replacement of the Cl in PhCCl:NPh by H by means of H<sub>2</sub>SnCl<sub>4</sub> in Et<sub>2</sub>O and decompn. of the Sn double salt of the resulting Schiff base with steam) did not work so smoothly with 3,4,5-(MeO)<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>CO<sub>2</sub>H (I); the decompn. of the Sn salt offered difficulties or at times the unchanged anilide was recovered. The reaction has been further studied with the imide chlorides of the *p*-toluidide and *p*-anisidide of I instead of the anilide in the hope that the *p*-substituent would increase the reactivity of the Cl. On heating the pptd. Sn salts with dil. HCl they dissolved completely but on cooling there sepd., instead of the expected aldehyde, deep yellow compds. (II) yielding with hot alkalis the colorless phenol-aldehyde-anilines (MeO)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>CH(OH)NHC<sub>6</sub>H<sub>4</sub>R (III), which with HCl give the intensely yellow HCl salts. The II are therefore without doubt the Sn double salts of the III, which are extraordinarily stable towards H<sub>2</sub>O and acids. On the other hand, the free III heated with the least possible excess of dil. HCl yield (MeO)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>CHO (IV) (30% in the case of the toluidide). The formation of difficultly decompd. compds. analogous to the II can be completely avoided by starting with the methyl- or benzylamide of I; the resulting Sn double salts smoothly yield IV with boiling dil. HCl, although in only somewhat more than 50% yield, as a part of the imide chloride polymerizes. 3,4,5-(PhCH<sub>2</sub>O)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>CCl:NPh gives a non-decomposable compd. and, moreover, the PhCH<sub>2</sub> groups are partly split off by the H<sub>2</sub>SnCl<sub>4</sub>; on the other hand, (BzO)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>CCl:NPh is reduced to the Schiff base, which on cleavage gives 3,4,5-(BzO)<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>CHO in cryst. form, m. 127-8° (decompn.). With PhCCl:NOH not only the Cl but the OH group also is smoothly replaced by H with formation of the Et<sub>2</sub>O-insol. benzalimide chlorostannate, (PhCH.NH)<sub>2</sub>H<sub>2</sub>SnCl<sub>4</sub> (VI), which seps. after several days; from PhCH:NOH it is obtained immediately. Me<sub>3</sub>C NOH yields an analogous compd. after several weeks while Ph<sub>3</sub>C:NOH is not reduced at all. (PhCCl:N—)<sub>2</sub> likewise yields VI; probably it is first reduced to PhCCl:NH. *O*-Trimethylgallic *p*-toluidide (11.7 g. from 12.5 g. of the chloride with MeC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> in Et<sub>2</sub>O), m. 154°. *O*-Trimethylgallic aldehyde-*p*-toluidine (III, R = Me), from the toluidide heated on the H<sub>2</sub>O bath with Et<sub>2</sub>O, followed by treatment of the resulting imide chloride (m. 108-9°) with H<sub>2</sub>SnCl<sub>4</sub> in Et<sub>2</sub>O and decompn. of the orange-yellow chlorostannate (m. 122-4° (decompn.)), m. 100-1°; HCl salt, intensely yellow, m. 90-1°, identical with the product obtained from IV and *p*-MeC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> with 14% HCl. *O*-Trimethylgallic *p*-anisidide (16.5 g. from 13 g. of the chloride), m. 158.5°; aldehyde-*p*-anisidine, through the imide chloride (m. 105-6°) and the red-orange chlorostannate (m. 192°), m. 108°, unchanged by long boiling with H<sub>2</sub>O or dil. NaOH, only partially decompd. by hot 2 N HCl; HCl salt, orange-yellow, m. 153-4°. *O*-Trimethylgallic aldehyde-aniline-HCl, from IV, PhNH<sub>2</sub> and 24% HCl, intensely yellow, m. about 165°, dissolves in hot 24% HCl and seps. unchanged on cooling, is decompd. by about 15% HCl; free base, m. 91.5-2.0°. *O*-Trimethylgallic benzylamide (15 g. from 13 g. of the chloride), m. 140.5°; chlorostannate obtained from the imide chloride, light yellow, m. 180° (decompn.). Methylamide (15 g. from 15 g. of the chloride), m. 135°; chlorostannate, from the imide chloride, faintly yellow, m. about 125°. *O*-Tribenzylgallic anilide, from (HO)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>CONHPh, PhCH<sub>2</sub>Cl and KOH in boiling alc. in H, m. 178-9°; the imide chloride with H<sub>2</sub>SnCl<sub>4</sub> in Et<sub>2</sub>O

slowly dissolves with the formation, in the course of several weeks, of a bright yellow chlorostannate, m 196°, which is colored blood red by  $H_2O$ , dissolves easily in dil NaOH, only on boiling in dil HCl (with deep yellow color), reprecipitated from both solns. in blood red form on neutralization, the HCl soln gives a transient dark green color with  $FeCl_3$ ; from concd HCl it partially seps again in yellow flocks on cooling. VI decomps 210–60°, soon evolves an odor of  $BzH$  in the air, dissolves at once in  $H_2O$  with sepn of  $BzH$  gives a brown ppt in alkalis with Nessler reagent, does not reduce Fehling soln. Acetone *insoluble* chlorostannate, m 219–20° to a foamy mass, gives an orange-yellow ppt. in alkalis with Nessler reagent. Benzophenone oxime chlorostannate, m about 140°, only very slightly sol in dil acids, sol without change in concd. HCl, reduces Fehling soln only after long boiling with dil HCl. C. A. R.

Some synthetic experiments with *O*-trimethylgallic aldehyde. ADOLF SONN, with ERNST MÜLLER, WOLFGANG BÜLOW and WALTER MEYER. *Ber.* 58B, 1103–10 (1925) cf preceding abstr.—Methyl [3,4,5-trimethoxybenzylidene]amine (28 g. from 28 g 3,4,5-(MeO) $_3$ C $_6$ H $_2$ CHO (I) and 2 mols 33% alc. MeNH $_2$ ), faintly yellow refractive oil, b $_p$  181–92°, reduced by colloidal Pd and H to the benzylamine (II), viscous, refractive oil, b $_p$  192°, absorbs CO $_2$  from the air, HCl salt, m 178°; Bz deriv, m 102°. 3,4,5-Trimethoxyacetophenone oxime, m 102°, is reduced by Na-Hg to (MeO) $_3$ C $_6$ H $_2$ CH(NH $_2$ )Me (Spath, C A 14, 1114), isomeric with II, b $_p$  173–4°, viscous refractive oil eagerly absorbing CO $_2$  from the air, HCl salt, m 214°, Bz deriv, m 152°. 3,4,5-Trimethoxy  $\omega$ -isonitrosoacetophenone (12 g. from 20 g (MeO) $_3$ C $_6$ H $_2$ COMe with Na and AmONO in alc), light yellow, m 95°, 5 g with SnCl $_4$  and fuming HCl gives 3 g 3,4,5-trimethoxy  $\omega$ -aminoacetophenone HCl, m 256° (foaming).  $\alpha$ -Benzoylamino- $\beta$ -3,4,5-trimethoxyphenylacrylic inner anhydride (2-phenyl-4,3',4',5'-trimethoxybenzylidene-5-oxazolone) (37 g. from 38 g I with hippuric acid and NaOAc in Ac $_2$ O), lemon yellow, m 194–5°, refluxed 3 hrs in 1% Na $_2$ CO $_3$ , 37 g of the anhydride gives 3.65 g. of the acid, m 184°, 6.5 g of which with Me $_2$ SO $_4$ -NaOH gives 3.2 g of the *N*-Me deriv, m 164°, reduced by Na-Hg to the propionic acid, (MeO) $_3$ C $_6$ H $_2$ CH(CO $_2$ H)NMeBz, m 118°.  $\alpha$ -Benzoylamino- $\beta$ -3-nitro-5-methoxy-4-acetoxyphenylacrylic inner anhydride (2-phenyl-4,3'-nitro-5'-methoxy-4'-acetoxybenzylidene-5-oxazolone) (37 g. from 6 g. nitrovanillin, hippuric acid and NaOAc in Ac $_2$ O), orange-red, m 230°; acid, yellow, m 233°.  $\beta$ -4,5-Dimethoxy-3-nitrophenylacrylic acid (2.5 g. from 3.6 g 3,4,5-O $_2$ N(MeO) $_3$ C $_6$ H $_2$ CHO, Ac $_2$ O and NaOAc at 180°), m 161°, reduced by FeSO $_4$  in boiling concd. NH $_4$ OH to the 3-amino acid whose HCl salt m 204° (decomps.). 3,6-Bis-3',4',5'-trimethoxybenzo-2,5-diketopiperazine (1.8 g from 2.4 g I, glycine anhydride and NaOAc in Ac $_2$ O at 120–30°), yellow, m 255–6°, sol in concd H $_2$ SO $_4$  with orange red color, 1 g in alc. suspension with Na-Hg gives 0.8 g of the bisbenzyl compd, m 230–1°. 2-Hydroxy-4,6,3',4',5'-pentomethoxychalcone (2.7 g. from 1.8 g 2,4,6-HO(MeO) $_3$ C $_6$ H $_2$ Ac, I and NaOH in alc), golden yellow, m 183°, sol in concd H $_2$ SO $_4$  with dark red color, gives in very dil. alc. soln a red brown color with  $FeCl_3$ , 2.7 g refluxed in alc with aq HCl gives 1.15 g of the flavone (MeO) $_3$ C $_6$ H $_2$  CO CX CH[C $_6$ H $_3$ (OMe) $_3$ ] O (X = H), m. 173–4°, sol. in

conc'd H $_2$ SO $_4$  with faint yellow color, 1 g of which in boiling alc. with AmONO and HCl gives 0.2 g of the isonitroso deriv. (X = .NOH), yellow, m. 210–1° (decomps.), sol. in conc'd H $_2$ SO $_4$  with orange-yellow color and green fluorescence, converted by boiling in AcOH with 10% H $_2$ SO $_4$  into myricetin penta-Me ether, yellow, m 230°, sol in conc'd H $_2$ SO $_4$  with yellow color. C. A. R.

$\beta$ -Piperonylpropionitrile and some derived substances. WILSON BAKER and ROBERT ROBINSON. *J. Chem. Soc.* 127, 1421–33 (1925).— $\beta$ -Piperonylpropionitrile (I), b $_p$  186–7°, m 33°, by thermal decomps of  $\alpha$ -cyano- $\beta$ -piperonylpropionic acid in the presence of Cu powder; H $_2$ SO $_4$  gives a deep crimson color, becoming olive-green on diln with H $_2$ O and heating. Oxidation with H $_2$ O $_2$  gives the amide, m 123.5°. Nitration of I gives the 6-NO $_2$  deriv. (II), pale honey-color, m 113°; heating with dil aq NaOH causes the evolution of NH $_3$  and gives a deep crimson soln, which gives an olive-green color with  $FeCl_3$ . II with conc'd HCl gives  $\beta$ -6-nitropiperonylpropionic acid, yellow, m 167–3.5°. Reduction of II with Sn and HCl appears to give ethylaminopiperonyl- $\omega$ -carboxylic anhydride (Perkin, *J. Chem. Soc.* 59, 159 (1891)). Na and EtOH reduce I to  $\gamma$ -piperonylpropylamine (III), highly refracting liquid, b $_p$  160–1°, d $_4^{20}$  1.141 (yield, 83%), carbonate, m 92–4°; HCl salt, m 206–8°, Ac deriv, m 89°. III and piperonal give piperonylidene- $\gamma$ -piperonylpropylamine, m 79.5°. III, MeI and EtONa give  $\gamma$ -piperonylpropyltrimethylammonium iodide, m 146°, Ag $_2$ O gives the hydroxide, which, at 160°, decomps. into H $_2$ O, Me $_3$ N and isosalrole, the yield being 60% of the iodide and 21% of the piperonal. I and m C $_6$ H $_5$ (OH) $_2$  in Et $_2$ O, sat'd with HCl at 0°, give homopiperonylresacetophenone (IV), m 130°; heated with Ac $_2$ O and ZnCl $_2$ , the resulting soln.


has an intense yellowish green fluorescence. *Mono-Me ether*, m. 89–90°, gives a reddish violet color in EtOH with FeCl<sub>3</sub>, heated with Ac<sub>2</sub>O and ZnCl<sub>2</sub>, the red soln. exhibits intense ivy-green fluorescence. Ac<sub>2</sub>O and AcONa did not give a chromone deriv. IV, Ac<sub>2</sub>O and AcONa give the *Ac deriv.* m. 101.5° (changing to the  $\beta$ -modification, m. 119.5°) of 7-hydroxy-3-homopiperonyl 2-methylchromone, m. 214–5° (changing into the  $\beta$ -form, m. 222–3°), whose alk. soln. exhibits a bluish violet fluorescence. *Me ether*, m. 124–5°, whose *dibromide* is a yellow powder becoming orange on keeping, darkens 155°, m. to deep red liquid above 170°. The H<sub>2</sub>SO<sub>4</sub> soln. is reddish purple but rapidly becomes brown, gray, olive gray and then brown. On boiling with EtOH there result pink needles, C<sub>15</sub>H<sub>13</sub>O<sub>2</sub>Br, m. 206–7°, which are stable to hot EtOH-KOH for a short time and with Ac<sub>2</sub>O and ZnCl<sub>2</sub> give a carmine soln. with intense yellowish green fluorescence.  $\alpha$ -Cyano- $\beta$ -veratrylacrylic acid, pale yellow, m. 201–2°, crystals with 1 MeOH in long grayish violet needles of metallic appearance, reduction gives the corresponding propionic acid, m. 139°.  $\beta$ -Veratrylpropionitrile, pale yellow oil, b<sub>7</sub> 194–5°, m. 46.5° (yield, 70%). Homoveratrylresacetophenone m. 146–7° (22% yield), 7-Hydroxy-3-homoveratryl-2-methylchromone m. 153–4° (90% yield), *Ac deriv.* m. 140.5°, *Me ether* m. 108°.

Oxidations in turpentine and olive oil. ERNEST WALKER *J. Chem. Soc.* 127, 1491(1925).—Oxidation of org. compds. may be carried out in turpentine which has been exposed to the air for some time or in rancid olive oil (fresh oil is made rancid by bubbling air through it for 24 hrs. at about 70°, the oil being a pale green or almost colorless). Thus, Ph<sub>3</sub>AsCl or the oxide gives Ph<sub>3</sub>AsO<sub>2</sub>H; (ClCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>S gives the sulf-oxide.

Rotatory power and dispersion in the terpene series. PARISELLE. *Compt. rend.* 180, 1832–3(1925).—In the prepn. of camphene by a method already described (*C. A.* 17, 3176), the use of *d*-, *l*- or *dl*-pinene will yield a camphene having the corresponding configuration. Thus  $\alpha$ -pinene from Bordeaux oil gave camphene with  $[\alpha]_D$  –79.90°, while that from Alep oil gave camphene with  $[\alpha]_D$  77.10°. Both camphenes m. 45–6°, b<sub>7</sub> 52°, n<sub>D</sub> 1.58°, and had the same dispersion in Et<sub>2</sub>O. Addn. compds. with H, Br, HCl, HBr and HCO<sub>2</sub>H were prepd. from each camphene, and the value of  $\alpha$  and the dispersion with different wave lengths detd. *Derivs. of d-camphene* ( $[\alpha]_D$  77.10°). *Hydride*, prepd. by the method of Vavon (*C. A.* 4, 1478), m. 59–61°, b<sub>7</sub> 62–3°,  $[\alpha]_D$  –4.50°, gave dispersions of 1, 1.18 and 1.96 for 589, 546 and 436 A.U., resp. *Bromide*, from Br and camphene in CCl<sub>4</sub> at 0°, m. 89–91°,  $[\alpha]_D$  –71° with dispersions of 1, 1.18 and 2 for 589, 546 and 436 A.U., resp. *HCl salt*, from dry HCl and camphene, can be crystd. from EtOH satd. with HCl, unstable m. 138–40°,  $[\alpha]_D$  –41.2°, with dispersions of 1, 1.045, 1.19, 1.53, 2 and 2.4 for 589, 578, 546, 492, 436 and 404 A.U., resp. *HBr salt*, prepd. like the HCl salt and had the same dispersions,  $[\alpha]_D$  –62.3°. By the action of 98% HCO<sub>2</sub>H on camphene in the presence of C<sub>6</sub>H<sub>5</sub>(CO)<sub>2</sub>O, was quant. obtained *bornyl formate*, b<sub>14</sub> 95°, d<sub>20</sub> 1.01, n<sub>D</sub><sup>20</sup> 1.470,  $[\alpha]_D$  –3.14°, with dispersions of 1, 1.038, 1.18, 1.52, 1.98 and 2.38 for 589, 578, 546, 492, 436 and 404 A.U., resp. *Derivs. of l-camphene* ( $[\alpha]_D$  –79.90°). The *hydride*, *bromide*, *HCl* and *HBr salts* were prepd. in the same way as those of *d*-camphene and had the same dispersions. The results show that the *rotatory power of all addn. compds. of camphene* is of opposite sign to that of the original camphor, while their dispersions, though very close to those of  $\alpha$  pinene, are much lower than those of camphene. Probably modifications of the camphene nucleus are involved in the formation of the addn. compds., this is in accordance with the work of Langlois (*C. A.* 14, 937), who has shown the ease with which camphene forms abnormal compds. by migrations in the mol.

C. C. DAVIS

Action of chlorine on  $\alpha$ -pinene. GEORGES BRUS. *Compt. rend.* 180, 1507–9 (1925).—By the action of Cl on pinene, d. 0.860,  $[\alpha]_D$  48.1°, n<sub>D</sub><sup>15</sup> 1.458, were obtained bornyl chloride, liquid di-Cl deriv., a cryst. di-Cl deriv., C<sub>10</sub>H<sub>16</sub>Cl<sub>2</sub>, m. 170°, and small quantities of poly-Cl derivs. C<sub>14</sub>H<sub>20</sub>Cl<sub>2</sub>, large monoclinic crystals, faces *p*(001) *m*(110) dominant; *h*<sup>1</sup>(100) *a*<sup>1</sup>(101) *g*<sup>1</sup>(010) little developed,  $a:b:c = 1.337:1:1.384$ ;  $\beta$ (Ox, Oz) = 121.42°. Calcd. and observed angles of the normals are given. Aniline and powd. Zn, Mg, and Cu in alc. have no action on this compd. It is tricyclic chloride,

CH<sub>2</sub>  
Cl  Cl, resulting from a mol. transposition similar to that taking place in the

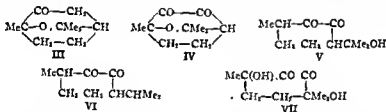
formation of bornyl chloride from the tertiary HCl salt. MARGARET W. McPHERSON

Use of nopinene for the manufacture of terpene hydrate and terpineol. GEZA ATSTERWEIL. *Perfumery Essent. Oil Rec.* 16, 157–8(1925).—Nopinene or  $\beta$ -pinene

has only very recently been used on a manufg scale, especially in the production of terpineol and camphor. Following Wallach's procedure, it appears that the hydration of nopinene to terpene hydrate, and on this account, the manuf of terpineol is technically more advisable than the manuf of these products from  $\alpha$ -pinene or turpentine spirit. Moreover, the terpene hydrate thus obtained seems to give a terpineol of much more delicate lilac odor than that resulting from  $\alpha$  pinene. The industrial sepn. of the 2 turpentine constituents,  $\alpha$  pinene and nopinene, is now an accomplished fact.

W. O. E.

The cineole group. VI. Relations between diketocineole and buccocamphor. G. CUSMANO AND G. MASSA. *Gazz. chim. ital.* 55, 140-8(1925).—The resistance of the camphanic bridge,  $-\text{CMe}_2-$ , to chem. reagents diminishes with the change of camphor (I) into camphorquinone (II). With concd  $\text{H}_2\text{SO}_4$  I gives carbenone at  $102-3^\circ$ , while II at  $0^\circ$  gives camphorisquinone. Similarly in continuing the study of the cineole group (C. A. 6, 1138, 14, 169, 171, 3476; 17, 2877); it was found that the cineolic bridge,  $-\text{O}-\text{CMe}_2-$ , becomes less stable on converting ketocineole (III) into diketocineole (IV). Thus while III cannot be reduced by  $\text{Zn} + \text{H}_2\text{SO}_4$  or by  $\text{Al-Hg} + \text{H}_2\text{O}$ , IV treated similarly adds 2 H atoms, giving an 8 hydroxybuccocamphor (V), a position isomer of a compd. recently obtained by C. (C. A. 17, 2280, 19, 55). The relation between IV and buccocamphor (VI) was also detd. in another way. On treating IV with dry HBr at  $40-50^\circ$  was formed a dibromobuccocamphor which with  $\text{Zn} + \text{EtOH}$  easily gives VI. Five g IV in 15 cc  $\text{H}_2\text{O} + 1$  cc concd.  $\text{H}_2\text{SO}_4$  were treated with Zn dust. An insol. product that made the Zn dust stick together was pptd.  $\text{Et}_2\text{O}$  was added and the reduction continued until the  $\text{Et}_2\text{O}$  layer became nearly colorless. The  $\text{Et}_2\text{O}$  layer was then worked up. The product,  $\text{C}_{15}\text{H}_{24}\text{O}_4$ , seps. as colorless crystals, m.  $78-9^\circ$ , and was shown to be V. V was also obtained from IV by treating the  $\text{Et}_2\text{O}$  soln with  $\text{Al-Hg}$ . VII (C. A. 19, 55) treated with alkali adds  $\text{H}_2\text{O}$  and gives 2 acids having 10 C atoms. Two g. V in 5 cc.  $\text{H}_2\text{O} + 1$  g KOH (or  $\text{Be}(\text{OH})_2$ ) on the  $\text{H}_2\text{O}$  bath evolved an odor of  $\text{Me}_2\text{CO}$ , which was also condensed and identified. The alk. soln. was cooled, filtered, satd. with  $\text{CO}_2$  and extd. with  $\text{Et}_2\text{O}$ . The  $\text{Et}_2\text{O}$  soln. contained 1 methyl-2,3-diketohexamethylene (Wallach, C. A. 13, 425). The alk. aq. soln. was acidified and on extg. with  $\text{Et}_2\text{O}$  gave 1-methyl-2-hydroxy-2-carboxycyclopentane. V in  $\text{Et}_2\text{O}$  was satd. with dry HBr. After some hrs. the mixt. was washed with  $\text{H}_2\text{O}$ ,



the solvent was evapd., and the oily residue (b. about  $270^\circ$  and contains no Br) was found to be methylisopropylpyrocatechol previously obtained from VII by a different reaction mechanism.

E. J. W.

Oxidations with ozone. II. Preparation of camphor. E. BRINER, T. EGGER AND H. PAILLARD. *Helv. Chim. Acta* 7, 1018-22(1924); cf. C. A. 18, 1824.—When borneol is treated with  $\text{O}_3$  in the manner described in the former paper (*loc. cit.*) camphor is obtained. The proportion of  $\text{O}_3$  actually utilized in oxidation reaches 92.7% under the most favorable conditions, viz. in hexane soln. at  $-80^\circ$  with  $\text{O}_3$  of 8.5% strength by vol. At higher temps., although the borneol is satisfactorily oxidized, much  $\text{O}_3$  is lost, partly by decompn. in the app. and partly because further oxidation takes place, mainly to camphoric acid. The loss of  $\text{O}_3$  in bubbling through the solvent depends mainly on the temp. and to a lesser degree on the concn. of the  $\text{O}_3$ . Thus with 4.1% (vol.)  $\text{O}_3$  33-9% is decompd. in bubbling through  $\text{CCl}_4$  at  $20^\circ$ , but only 6.4% in the same solvent at  $-20^\circ$  and only 1.9% in hexane at  $-70^\circ$ , with 13.2% (vol.)  $\text{O}_3$  the figures are 42.1, 8.7, and 2.1%, resp. Isoborneol is oxidized just as readily, the yield (on the  $\text{O}_3$ ) being about 10% less. Camphene gives no camphor when oxidized in soln. (cf. Harries and Pallen, C. A. 4, 2488) nor when it is vaporized; Nordheim's statement (Ger. 64,180) is thus not confirmed. Camphor was satisfactorily detd. in such mixts. as were obtained in the above expts. by Fuller's method (C. A. 5, 3610) using  $\text{NH}_2\text{OH}$ . B. C. A.

Action of *p*-anisylmagnesium bromide and *p*-tolylmagnesium bromide on camphor.

S. LEDUC. *Compt. rend.* 180, 1502-3(1925)—Phenylborneol and benzylborneol were obtained from camphor and the appropriate Grignard reagents by Haller and Bauer (cf. *Compt. rend.* 149, 677(1906)). Leduc increased the yield of phenylborneol from 25 to 40% by working at room temp. Anisylcamphene,  $C_{15}H_{18}.CH:CC_6H_4OMe$ , m.

85°, and a little diamsyl were formed from camphor and  $p\text{-MeOC}_6\text{H}_4\text{MgBr}$ . The oil accompanying the camphene crystals (also anisylcamphene) mostly b<sub>10</sub> 178-180°. No anisylborneol was obtained, the camphene being formed by the dehydration of the borneol. Yield, 20-30% of the theory. The camphene decolorizes Br but gives no cryst. Br deriv., nor any crystals upon treatment with HBr in acid soln. An oil, b<sub>11</sub> 154-7°, is obtained in low yield from camphor and  $p\text{-MeC}_6\text{H}_4\text{MgBr}$ . Analysis gave values intermediate between those of the tertiary tolylborneol and the tolylcamphene.

MARGARET W. McPHERSON

The rotatory power of certain camphor derivatives. A. HALLER AND RENÉ LUCAS. *Compt. rend.* 180, 1803-6(1925)—The work was carried out with the object of detg. a relation between the chem. compn. and the value of  $\alpha$  and the influence of the solvent on  $\alpha$ . The detns. were made with a Jobin polarimeter at about 19°, with radiation from Hg, Na and Li arcs. Data are tabulated of values of  $\lambda$  of 4358, 4602, 5460, 5780, 5893, 6203 and 6708 Å. U. for benzylidene-, benzylidene *o* chloro-, anisylidene-, piperonylidene-, benzyl-, anisyl- and piperonylcamphor, the first 4 in EtOH and in  $C_6H_6$  and the last 3 in EtOH, in  $C_6H_6$ , in  $CS_2$  and in  $C_4H_8$ . There was a difference in the values of  $\alpha$  of 5-6% in EtOH and in  $C_6H_6$  for the first 4 compds., while in the last 3 compds. it was considerably greater and more variable. The data show in general that the rotatory power varies over a large range with the solvent, but that the expression  $([\alpha]_{C_6H_6} - [\alpha]_{EtOH})/([\alpha]_{C_6H_6} - [\alpha]_{CS_2})$  is nearly const., even for different wave lengths, being 0.560-0.596 for benzyl-, 0.613-0.636 for anisyl- and 0.495-0.540 for piperonylcamphor. For the expression  $[\alpha]_{C_6H_6} - [\alpha]_{CS_2}$  alone the values are more nearly const., still, and a comparison of  $\alpha$  for mixts. of  $C_6H_6$  and  $CS_2$  indicates that there are 2 differing active forms and that, as shown by Darmoni this constancy is a result of the law of Biot for mixts. of 2 active compds. The results are also similar to those found for tartaric and malic acids.

C. C. DAVIS

Rotatory dispersive power of organic compounds. XVI. Halogen derivatives of camphor. Optical superposition in the camphor series. J. O. CUTTER, HENRY BURGESS AND T. M. LOWRY. *J. Chem. Soc.* 127, 1260-74(1925); cf. *C. A.* 19, 1702.—A study is made of the influence on the rotatory power of camphor and on its rotatory dispersion of the creation of a new asym. C atom by the introduction of a halogen in the  $\alpha$ - or  $\alpha'$ -position. Measurements are reported, over a range of wave lengths, of the optical rotations of  $\alpha$ - and  $\alpha'$ -chloro- and of  $\alpha$ -,  $\alpha'$ - and  $\beta$ -bromocamphor and of 5 isomeric dibromocamphors. For  $\alpha$ - and  $\alpha'$ -chlorocamphor,  $[\alpha]_{441} = 65.5^\circ = 24.6^\circ$  or  $[M]_{441} = 111.8^\circ = 41.9^\circ$ ; for  $\alpha$ - and  $\alpha'$ -Br derivs.,  $[\alpha]_{441} = 51.8^\circ = 98.9^\circ$  and  $[M]_{441} = 111.5^\circ = 212.6^\circ$ ; for  $\alpha,\beta$ - and  $\alpha'\beta$ -dibromocamphor,  $[\alpha]_{441} = 8.8^\circ = 91.9^\circ$  and  $[M]_{441} = 25.7^\circ = 270^\circ$ . The behavior of the  $\pi$ -derivs. is shown to be altogether exceptional. In 9 cases out of the 10, the curves of rotatory dispersion are complex but normal, i. e. the rotation increases progressively as the wave length diminishes, giving rise to quasi-hyperbolic dispersion curves, which do not exhibit any obvious anomalies; the dispersion is, however, not simple, since it cannot be represented by a single term of Drude's equation. The dispersion can usually be represented by 2 terms of the Drude equation; but in the case of  $\alpha',\beta$ -dibromocamphor (where all the rotations are —) imaginary values are obtained for the consts. in such an equation, showing that the dispersions are of still greater complexity. In the case of  $\alpha'$ -bromocamphor, the negative term predominates over the positive term in the visible region, but a reversal of sign is observed in the early ultra-violet region; the dispersion is therefore not merely complex but definitely anomalous. An inflection at 5455 Å. U., max. at 4710 and reversal of sign at 3890 have all been observed exptly. All rotations are reported in  $C_6H_6$  solns.

C. J. WEST

Formation of *d*-2,2,4-trimethylcyclohexan-3-one-1-carboxylic acid from *d*-camphorquinone. C. STANLEY GIBSON AND JOHN LIONEL SIMONSEN. *J. Chem. Soc.* 127, 1294-303(1925); cf. Manasse and Samuel, *Ber.* 30, 3157, 35, 3331.—The action of  $H_2SO_4$  on *d*-camphorquinone (M. and S.) gives *d*-2,2,4-trimethylcyclohexan-3-one-1-carboxylic acid (I), m. 71-2°,  $[\alpha]_{441}^{15} 47.4^\circ$  (EtOH,  $c$  1.0346) and for a 2nd fraction, 18.7° ( $c$  0.9626); in a very slight excess of aq. NaOH  $[\alpha]_{441}^{15} 22.2^\circ$  ( $c$  0.9784), changing after 48 hrs. to 15.1°, and for the 2nd fraction, 8.1° and 5.1°. Semicarbazone, m. 228-9°;  $\alpha$ -oxime, m. 164-5°; in EtOH-AcONa, the  $\beta$  oxime, m. 226° (decompn.). results. Me ester (II)

m  $82-3^{\circ}$ , a 2nd fraction  $b_p$   $135-40^{\circ}$  and is probably an equil. mixt. of the keto and enol forms, *oxime* m  $110-1^{\circ}$ .  $\alpha$ -Semicarbazone, decomps.  $231^{\circ}$  (70% yield),  $[\alpha]_{D}^{25} -55.8$  (AcOH,  $c$  0.9540), changing after 48 hrs. to  $-50.5^{\circ}$ ;  $\beta$ -semicarbazone, m  $161-2^{\circ}$ ,  $[\alpha]_{D}^{25} -38.2^{\circ}$  (AcOH,  $c$  1.0464), rising to a max. at  $53.5^{\circ}$  and giving the equil. value of  $-50.2^{\circ}$ . In EtOH,  $\alpha_{445}$  is  $-0.73^{\circ}$  ( $c$  0.9896) and does not change in 24 hrs. Hydrolysis of both forms gives a mixt. of solid and liquid II. Oxidation of I with  $HNO_3$  gives  $\beta$ -methylpentane- $\beta,\gamma,\gamma$ -tricarboxylic acid (Perkin and Thorpe, *J. Chem. Soc.* 85, 135 (1904)). Reduction of I (M. and S.) gives *trans-d* 3-hydroxy-2,2,4-trimethylcyclohexane-1-carboxylic acid,  $[\alpha]_{D}^{25} 43.6^{\circ}$  (EtOH,  $c$  1.0146); *Me ester*,  $b_p$   $150-2^{\circ}$ . The ester, treated with  $PCl_5$  and then  $distd$ , finally being heated with  $PhNEt_3$ , gives *Me 1,2,4-trimethyl- $\Delta^4$ -cyclohexene-1-carboxylate*,  $b_p$   $105-7^{\circ}$ , fragrant-smelling oil, the free acid  $b_p$   $150-2^{\circ}$ ,  $[\alpha]_{D}^{25} -38.5^{\circ}$  (EtOH,  $c$  2.653); it absorbs Br rapidly but the Br acid decomps. with evolution of  $HBr$ .  $NH_4$  salt, decomps.  $147-8^{\circ}$ ; the Ca, Ba and Ag salts are sparingly sol. in  $H_2O$ . There also results some II in the above reaction.

C. J. WEST

**Synthetic catalysts.** GUMO CUSMANO *Gazz. chim. ital.* 55, 218-24 (1925).—In 2 previous papers (*C. A.* 13, 1587; 15, 838), C. found that the catalytic action of camphor on the reaction  $SO_2 + Cl_2 \rightarrow SO_2Cl_2$  is not a contact reaction but is due to the residual affinity of its O. It was found that other org. compds. having a CO,  $CO_2H$  or ether function also act as catalysts. A  $NO_2$  group, a free  $SO_2H$  group or a substituted halogen atom in the compds. acts anticatalytically and stops the catalysis. The C skeleton must be resistant to chlorination.  $\alpha$ -Diketones (like diketocycloole (I) ( $R = R' = H$ )) were inactive as catalysts while  $\beta$  and  $\gamma$ -diketones favored the synthesis. In the case of I the residual affinities of the CO groups involved in the catalysis presumably influence each other while if they are more distant from each other they bring about the catalysis. C. has undertaken to study the action of a series of compds. I ( $R = O$ ,  $R' = H$ ;  $R = O$ ,  $R' = NOH$ ,  $R = R' = NOH$ ) and II as catalysts in this reaction. The use of



these substances is also discussed from the standpoint of selective catalysis as recently developed in the case of Pt (Vavon, Husson, *C. A.* 16, 3792, Rosenmund, *C. A.* 15, 2435; Ipatiew, *C. A.* 5, 801). The data on the prepn. of these catalysts and their influence on this reaction will be described in later papers.

E. J. WITZEMAN

The action of methylmagnesium iodide on esters of  $\alpha$ -monocamphoronitrile. A. HALLER AND F. SALMON-LEGAGNET *Compt. rend.* 180, 1621-3 (1925); cf. *C. A.* 19, 1703.—Various esters of the general formula  $C_{10}H_{17}(CN)CO_2R$  (I) have been prep'd.; where R is Ph I, m  $76-7^{\circ}$ ,  $[\alpha]_D^{25} 20^{\circ}27'$  in  $C_6H_6$ ; *o*-tolyl (II), m  $99-100^{\circ}$ ,  $[\alpha]_D^{25} 25^{\circ}07'$  in  $C_6H_6$ ; *p*-tolyl, m  $96-7^{\circ}$ ,  $[\alpha]_D^{25} 28^{\circ}53'$  in  $C_6H_6$ ; benzyl,  $b_p$   $223^{\circ}$ ,  $[\alpha]_D^{25} 59^{\circ}24'$  in abs. alc.,  $[\alpha]_D^{25} 56^{\circ}31'$  in  $C_6H_6$ . With 5 mols. of  $MeMgI$  in  $Et_2O$  II reacts normally with formation as final product of the tert. alc. 1-[ $\alpha$ -hydroxy-*sec*-propyl]-1,2,2-trimethyl-3-cyanocyclopentane (III), m  $93-4^{\circ}$ ,  $[\alpha]_D^{25} 78^{\circ}15'$  in abs. alc.; a small amt. of a substance (IV) m  $164^{\circ}$  is also formed. The Me ester of I in  $Et_2O$  also reacts to give the above products, but in dry toluene the CN is attacked, the final product being 1-[ $\alpha$ -hydroxy-*sec*-propyl]-1,2,2-trimethyl-3-acetylcyclopentane, m  $95-6^{\circ}$ ; semicarbazone, m  $221-2^{\circ}$ . If after decomps. with  $H_2O$  the toluene be  $distd$ . off instead of  $evapd$ , the main product is IV, apparently 1-isopropenyl-1,2,2-trimethyl-3-acetylcyclopentane,  $b_p$   $144-5^{\circ}$ , m  $164^{\circ}$ , *oxime*, m  $103-4^{\circ}$ ; semicarbazone, m  $229-30^{\circ}$ ,  $[\alpha]_D^{25} 40^{\circ}44'$  in abs. alc.  $KMnO_4$  oxidation of IV yields 1,3-diacetyl-1,2,2-trimethylcyclopentane,  $b_p$   $151-6^{\circ}$ ; semicarbazone, m  $304-5^{\circ}$ .

WM. B. PLUMMER

Alcohols of the hydroaromatic and terpene series. IV.  $\alpha$ - and  $\beta$ -Fenchyl alcohols and some esters derived therefrom. JOSEPH KENYON AND H. E. M. PRISTON *J. Chem. Soc.* 127, 1472-87 (1925).—*d*-Fenchone, reduced with Na and  $EtOH$ , gives a mixt. of  $\alpha$ - (I) and  $\beta$ -fenchyl alcs. (II); I is isolated through the acid phthalate, m  $146^{\circ}$ ,  $[\alpha]_D^{25} 21.6^{\circ}$ ,  $27^{\circ}$  and  $65.2^{\circ}$  for  $\lambda$  5893, 5461 and 4359 (5% in  $EtOH$ ); I  $b_p$

86°, m. 47,  $d_{4}^{20} 1.09226$ ,  $[\alpha]_{D}^{20} -15.04^\circ$ ,  $-15.37^\circ$  (EtOH),  $-6.70^\circ$  (CS<sub>2</sub>). Mg salt, m. 290–5°. *p*-Nitrobenzoate, pale yellow, m. 108–9°;  $[\alpha]$  in 5% solns. in C<sub>6</sub>H<sub>6</sub> and CS<sub>2</sub>:  $-13.9^\circ$  and  $-16.1^\circ$ ,  $-17.4^\circ$  and  $20.0^\circ$ ,  $-18.0^\circ$  and  $-21.9^\circ$ ,  $-19.6^\circ$  and  $-23.2^\circ$ ,  $-29.5^\circ$  and  $-35.4^\circ$  for  $\lambda$  6708, 5893, 5780, 5461 and 4359. *p*-Chlorobenzoate, m. 73–4°. The mother liquors from I were changed into the Mg salt, the most sol. fractions of which gave II, which was purified through the *p*-nitrobenzoate, pale yellow, m. 82–3°;  $[\alpha]$  in 5% solns. in C<sub>6</sub>H<sub>6</sub> and CS<sub>2</sub>:  $8.2^\circ$  and  $10.3^\circ$ ,  $10.5^\circ$  and  $13.5^\circ$ ,  $11.4^\circ$  and  $14.8^\circ$ ,  $13.5^\circ$  and  $17.7^\circ$ , and  $23.6^\circ$  and  $28.4^\circ$  for  $\lambda$  6708, 5893, 5780, 5461, 4359. II,  $b_{11} 91^\circ$ , m. 3–4°,  $d_{4}^{20} 0.9605$ ,  $[\alpha]_{D}^{20} -27.97^\circ$ ;  $-26.23^\circ$  (5% in EtOH),  $-38.27^\circ$  (5% in CS<sub>2</sub>). Hydrogen phthalate, m. 153°,  $[\alpha]$  (5% in EtOH),  $7.5^\circ$ ,  $10.3^\circ$ ,  $11.3^\circ$ ,  $13.3^\circ$  and  $26.3^\circ$  for  $\lambda$  6708, 5893, 5780, 5461 and 4359. The following esters of I were prepd, values for  $n$  and  $[\alpha]$  being given for the homogeneous substance for several wave lengths and  $[\alpha]$  for solns. in EtOH and CS<sub>2</sub>. Formate,  $b_{11} 97^\circ$ ,  $d_{20}^{20} 0.9902$  (this order is followed for the other esters); acetate,  $b_{11} 99^\circ$ , 0.9695; propionate,  $b_{11} 115^\circ$ , 0.9614; butyrate,  $b_{11} 127^\circ$ , 0.9522; valerate,  $b_{11} 135^\circ$ , 0.9453; hexoate,  $b_{11} 152^\circ$ , 0.9400; heptate,  $b_{11} 160^\circ$ , 0.9338; octoate,  $b_{11} 176^\circ$ , 0.9277; nonoate,  $b_{11} 185^\circ$ , 0.9235; laurate,  $b_{11} 207-9^\circ$ , 0.9160; myristate,  $b_{11} 190-5^\circ$ , 0.9092. Esters of II: Formate,  $b_{11} 83.5^\circ$ , 0.9933; acetate,  $b_{11} 90^\circ$ , 0.9694; propionate,  $b_{11} 102^\circ$ , 0.9601; butyrate,  $b_{11} 112^\circ$ , 0.9531. *1*-Bornyl esters: Formate,  $b_{11} 94^\circ$ ; acetate,  $b_{11} 103^\circ$ ; propionate,  $b_{11} 114^\circ$ ; butyrate,  $b_{11} 125^\circ$ ; valerate,  $b_{11} 136^\circ$ . *d*-Isobornyl formate,  $b_{11} 94^\circ$ ; propionate,  $b_{11} 119^\circ$ ; valerate,  $b_{11} 138^\circ$ ; *1*-isobornyl acetate,  $b_{11} 112^\circ$ ; butyrate,  $b_{11} 125^\circ$ , values for  $[\alpha]$  and  $n$  are given for  $\lambda$  6708, 5893, 5780, 5461 and 4359. When  $[\alpha]_{D}^{20}$  are plotted against the no. of C atoms in the growing acyl chain, 4 different types of curves are obtained. *Bornyl esters*: the 5 esters of this series lie on a smooth curve which falls steadily and fairly rapidly from the 1st member to the last. *Isobornyl esters*: the 1st member has a relatively low value; there is then a big jump to the 2nd member, after which the values for the remaining 3 members fall steadily but slowly;  *$\beta$ -Fenchyl esters*: the curve is similar in character to that given by the isobornyl esters except that the relatively low value for the 1st member of the series is not so pronounced and the values from the 2nd member onwards fall much more rapidly.  *$\alpha$ -Fenchyl esters*: these lie on a smooth curve which falls steadily from the 1st member to the last. There are, however, 3 notable exceptions—a pronounced exaltation is shown by the propionate and a 2nd pronounced exaltation by the heptate and the octoate.

C. J. WEST

Action of carbon disulfide on benzidine. G. ROSSI AND B. CECCHETTI. *Gazz. chim. ital.* 55, 97–9 (1925).—Borodin (1860) boiled benzidine (I) with CS<sub>2</sub> and EtOH and obtained according to Strakosch (*Ber.* 5, 240) thiocarbonylbenzidine (II), NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>.C<sub>6</sub>H<sub>4</sub>.NH<sub>2</sub>.C:S and S also obtained what he thought was an isomer of II.

Forty-nine g. I + 10 g. CS<sub>2</sub> and enough abs. EtOH to dissolve I were boiled. A solid which was largely sol. in boiling alc. sepd. The filtered soln. sepd. a cryst. compd. This treatment was repeated and gave a compd. III, C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>S, decomps. +200°. R. and C. consider III to be constituted of 2 mols. I and 1 mol. CS<sub>2</sub>, i. e. thiocarbonylbenzidine, (H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>.C<sub>6</sub>H<sub>4</sub>.NH<sub>2</sub>)<sub>2</sub>.CS.

E. J. WITZEMANN

"2,7,9,9-Tetrahydroxyfluorene." CH. COURTOT AND R. GEOFFROY. *Compt. rend.* 180, 1665–7 (1925).—The product (I) of fusion of fluorene 2,7-disulfonic acid with alkali, described by Schmidt, Retzlaff, and Haid (*C. A.* 6, 2753) as 2,7,9,9-tetrahydroxyfluorene, is considered to be 4,4'-dihydroxydiphenyl-2-carboxylic acid (II). I is now found to m. 281–2°, as does II. The *tri-Bz* deriv. (III) (analyses favor this rather than the B<sub>2</sub> deriv.) exists in two forms, (a) m. 153°, resolidifies, and again m. 270°; (b) (from PhNO<sub>2</sub>) m. 287°. III from I or II, or a mixt. of these, shows the same behavior. Both I and II give with CaO (*p*-HOC<sub>6</sub>H<sub>4</sub>)<sub>2</sub> and show 3 replaceable H's; they have also the same ultra-violet absorption spectra. Also, both give with PCl<sub>5</sub> 2,7,9,9-tetrachlorofluorene. Both give with ZnCl<sub>2</sub> 2,7-dihydroxyfluorenone, m. 338°; dibenzoate, m. 241°; oxime, m. 300°. 2-Fluorenesulfonic acid gives on alk. fusion 4-hydroxydiphenyl-2-carboxylic acid, m. 180°, converted by ZnCl<sub>2</sub> to 2-hydroxyfluorenone, m. 211°.

B. H. NICOLET

Synthesis of 9-fluorenylamines. C. COURTOT AND P. PETITCOLAS. *Compt. rend.* 180, 297–9 (1925).—The extreme mobility of a halogen atom in the 1-position of indene and indan derivs. (cf. *C. A.* 18, 252, 1285) is shown also by a halogen atom in the 9-position of fluorene. With anhyd. NH<sub>3</sub>, 9-chlorofluorene reacts peculiarly, giving difluorenylamine (cf. Curtius and Kof, *C. A.* 7, 774), dibiphenylenethene, and traces of primary amine. With aliphatic or aromatic amines, however, the reaction is expressed by: C<sub>13</sub>H<sub>9</sub>Cl + 2NH<sub>2</sub>R = C<sub>13</sub>H<sub>9</sub>NHR + NH<sub>2</sub>R.HCl. Fluorenylaniline,

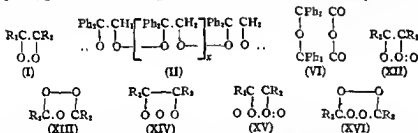
obtained from 9 chloro(or bromo)-fluorene and aniline, was prepd. by Staudinger and Gaulé (*C. A.* 11, 600). Fluorenyl *p*-tolylamine, similarly obtained, m. 124°. Fluorenyl-*p*-nitroaniline, yellow, m. 225°, and fluorenyl  $\alpha$ -naphthylamine, pink, m. 172°, were also prepd. Secondary fluorenylamines may be obtained also by reduction of the *N*-substituted ketimines of fluorenone (cf. Reddelien, *C. A.* 4, 3231) in alc.  $\text{NH}_4$ , this being sometimes preferable to the above method. Thus, 2-amino-9-chlorofluorene reacts in a complex manner with aniline, whereas reduction of the *aml* (orange, m. 141°) formed by condensation of 2-nitrofluorenone with aniline yields 2-aminofluorenylaniline, pale yellow, m. 151-2°.

B. C. A.

**Autoxidation of organic compounds. III. Autoxidation of asym-diphenylethylene.** H. STAUDINGER *Ber.* 58B, 1075-9(1925); cf. *C. A.* 8, 885.—This is also paper VI on highly polymerized compds. (cf. *C. A.* 19, 1245). According to the Engler-Bach theory, in autoxidations the  $\text{O}_2$  adds as a mol. The resulting mol-oxides (the term "peroxides" is reserved for compds of known structure and the name "mol-oxides" is used only when the structure of the primary autoxidation product is not known or when this primary product cannot be isolated) should in the case of  $\text{C}_6\text{H}_5$  derivs. be 4-membered ring structures (I) which should easily decomp. into 2 unsatd. compds  $\text{Ph}_2\text{C} \cdot \text{CH}_2$  under the influence of light chiefly takes up 1 mol.  $\text{O}_2$  with formation of a white amorphous mass, m. 131-2° (decompn.), which deflagrates on heating (with a weak explosion in larger amts), shows only little active O with  $\text{Ti H}_2\text{SO}_4$ , does not liberate I from KI, and does not decolorize indigo but catalytically accelerates polymerization processes (e. g. the polymerization of isoprene). On heating, it decomp. into  $\text{Ph}_2\text{CO}$  and  $\text{HCHO}$ , although not quant., as a small part of the  $\text{HCHO}$  undergoes further decompn.; the cleavage becomes quant. only on heating with  $\text{H}_2\text{O}$ . It is insol. in all solvents, gelatinizes in  $\text{C}_6\text{H}_6$  and forms, especially when impure, seemingly colloidal solns from which it can be completely removed, however, by centrifugalization. It does not affect the m. p. of  $\text{C}_6\text{H}_6$  or the b. p. of  $\text{CHCl}_3$ . It produces the impression of being a highly polymerized compd, which can be explained by assuming that, as the result of the tension a long open-chain structure (II) instead of the ring structure I has been formed. Other mol-oxides are known which, judging from their phys. properties, are also not monomol (those of dimethylsulvene,  $\text{Me}_2\text{C}:\text{CO}$ , malonic anhydride, the silylides, glycolides and ketene oxides). The peroxides hitherto isolated are not the primary autoxidation products; these, the monomol mol oxides, are certainly much richer in energy than the polymers and, on account of their instability, have not been isolated, they either polymerize or decomp. at once into 2 unsatd. compds.; in the autoxidation of  $\text{Ph}_2\text{C} \cdot \text{CH}_2$  there is always formed, even in the cold, some  $\text{Ph}_2\text{CO}$  and  $\text{HCHO}$ , which could not have been produced by decompn. of the II, for this is stable in the cold. Also, as shown in the following abstr., the primary mol-oxides may lose O and change into monoxides. In the case of  $\text{Ph}_2\text{C} \cdot \text{CH}_2$  such a monoxide (Klages and Kessler's diphenylethylene oxide, *Ber.* 39, 1753(1906)) could not be obtained under the most varied conditions by autoxidation or by heating II with an excess of  $\text{Ph}_2\text{C} \cdot \text{CH}_2$ . The fact that the relatively harmless II is not the primary product explains the explosions which sometimes occur in autoxidations of unsatd. compds; in an attempt to prep. II from about 10 g.  $\text{Ph}_2\text{C} \cdot \text{CH}_2$  and O under about 100 atm. by heating the steel bomb to 40-50° (there was no reaction in the cold) there occurred an explosion which completely destroyed the attached manometer and Cu capillaries.

**IV. Autoxidation of the ketenes.** H. STAUDINGER, K. DYCKERHOFF, H. W. KLEVER and L. RUZICKA. *Ibid.* 1079-87.—Also paper VII on highly polymerized compds and paper I on ketenes (cf. *C. A.* 18, 1284).  $\text{Me}_2\text{C}:\text{CO}$  on autoxidation at low temps. yields a peroxide (III) sepg. from  $\text{AcOEt}$  as a jelly, from  $\text{Et}_2\text{O}$  as a white powder which, when dry, is exceedingly explosive and detonates with great violence when touched, often even spontaneously; the small amts. clinging to the walls of the containers may be sufficient to shatter the latter. In  $\text{Et}_2\text{O}$  or  $\text{AcOEt}$  the decompn. proceeds harmlessly and at room temp. it goes on slowly, the products being  $\text{Me}_2\text{CO}$  and  $\text{CO}_2$  (the latter in 85-80% yield). No monoxide could be obtained either by autoxidation or under other conditions. From its phys. properties, complete insolv. and amorphous appearance, III must be a highly polymerized substance analogous to II. Unlike II, however, it liberates I from KI. With  $\text{Et}_2\text{C}:\text{CO}$  the autoxidation proceeds similarly, although more slowly; the resulting peroxide (IV), however, is more unstable than III. With the higher aliphatic ketenes it is often impossible to isolate the peroxide, as the velocity of formation is smaller than that of decompn. By working at -80° it is possible to obtain from  $\text{PhCMe}:\text{CO}$  a peroxide which, however, could not be thoroughly investigated on account of its instability; at room temp. the products of autoxidation are  $\text{PhCOMe}$ ,  $\text{CO}_2$  and a stable monoxide (V). From  $\text{Ph}_2\text{C}:\text{CO}$ , no peroxide can be obtained even at -80°;

as at room temp., the products are  $\text{Ph}_2\text{CO}$  and  $\text{CO}_2$ , polymeric ketene oxides and, finally, under certain conditions at a higher temp., *benzilide* (VI), which may be regarded as the dimeric monoxide; that the formation of VI is not due to abstraction of O from a mol-oxide by the excess of  $\text{Ph}_2\text{C}\cdot\text{CO}$  is shown by the fact that the yield of VI is the same whether an excess of ketene or of O is used. The ketene oxides form a mixt. of amorphous substances,  $(\text{C}_6\text{H}_5)_2\text{O}_2$ , which can be sep'd into a high melting substance (VII), insol. in  $\text{Et}_2\text{O}$  and  $\text{Me}_2\text{CO}$ , sol. colloiddally in  $\text{C}_6\text{H}_6$  and  $\text{CHCl}_3$ , a lower melting substance (VIII), sol. in  $\text{Et}_2\text{O}$  and  $\text{Me}_2\text{CO}$ , and mixts. of smary ketene oxides somewhat sol. in petroleum ether. All these products undergo the same decompns. with  $\text{H}_2\text{O}$  or  $\text{AcOH}$ , into  $\text{Ph}_2\text{C}(\text{OH})\text{CO}_2\text{H}$ ; with  $\text{MeOH}$ , into  $\text{Ph}_2\text{C}(\text{OMe})\text{CO}_2\text{H}$ , with  $\text{PhNH}_2$ , into  $\text{Ph}_2\text{C}(\text{NHPH})\text{CO}_2\text{H}$ . On higher heating, they in part undergo deep-seated decompn. and in part yield VI. The lower melting, more sol. ketene oxides are less stable and react much more rapidly (with  $\text{H}_2\text{O}$  or  $\text{MeOH}$ , e. g.) than the higher melting compds. V (yield, about 55%), amorphous, decomp.  $140-60^\circ$  (evolution of  $\text{CO}_2$ ), is probably a mixt. of polymeric monoxides. VII, decomp.  $200-10^\circ$  (evolution of  $\text{CO}_2$ ) on rapid, around  $150^\circ$  on slow heating, at high temps. the decompn. products are  $\text{Ph}_2\text{CO}$ ,  $\text{CO}_2$ , and  $\text{Ph}_2\text{CHCO}_2\text{H}$  but in  $\text{Et}_2\text{O}$  at  $150-60^\circ$  in a sealed tube it gives VI, together with  $\text{Ph}_2\text{CO}$  and  $\text{Ph}_2\text{CHCO}_2\text{H}$ . VII does not raise the h. p. of  $\text{CCl}_4$ . VIII begins to decomp.  $120-30^\circ$  on slow,  $180-80^\circ$  on rapid heating. *Diphenylmethoxyacetic acid*, from VII with  $\text{MeOH}$  at  $120^\circ$ , VIII and boiling  $\text{MeOH}$  or, best, from the smary non-cryst. ketene oxides and boiling  $\text{MeOH}$ , m.  $120-1^\circ$ , gives  $\text{Ph}_2\text{C}(\text{OH})\text{CO}_2\text{H}$  on long boiling with  $\text{AcOH}$ . VI, also obtained in 80-90% yield from  $\text{Ph}_2\text{CClCO}_2\text{H}$  or its Na salt heated 10 hrs. *in vacuo* at  $125^\circ$ , m.  $193-3.5^\circ$ , is much more stable towards  $\text{PhNH}_2$  and  $\text{AcOH}$  than the ketene oxides. V. Constitution of ozonides. H. STAUDINGER. *Ibid* 1088-98 — As shown in the preceding abstrs. for the  $\text{O}_3$  addn. products of unsatd. compds., so also the ozonides, both mono- and polymeric, hitherto isolated are in general only secondary products formed from unstable primary mol-ozonides; this assumption is necessary because the monomers, once isolated, cannot be converted into the polymers. Dicyclopentadiene in  $\text{AcOH}$  yields an easily sol. *diozonide* (IX) which is monomeric and easily undergoes fission. In  $\text{CCl}_4$ , on the other hand, is formed a wholly insol. *ozonide*



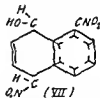
(X) which, from its phys. properties, must be highly polymerized and undergoes fission only with difficulty. Similar observations were made with dihydrodicyclopentadiene (XI). Where it can be proved with certainty that the isolated monomers are secondary products formed from the primary addn. products (XII), it would be advisable to call the former *iso-ozonides* instead of ozonides. The formulation XIII is suggested for these secondary products, which are believed to include the ozonides of all aliphatic  $\text{C}_6\text{H}_4$  derivs.; such a formulation agrees better with their properties than that (XIV) suggested by Harries. To the polymers is assigned a structure analogous to II. The primary ozonides may decomp., like the mol-oxides, with rupture of the 4-membered ring or they may lose  $\text{O}_2$  with regeneration of the  $\text{C}_6\text{H}_4$  deriv. The ox-ozonides are also secondary oxidation products of the XII which are assumed to take up 1 atom of O with formation of the unstable ox-ozonides (XV) which then rearrange into the iso-ox-ozonides (XVI). *Isodicyclopentadiene diozonide* (IX), from the diene in 10 parts  $\text{AcOH}$  treated 20 hrs. with 5%  $\text{O}_3$ , powder, m.  $95-8^\circ$  (decompn.), explodes on higher heating, very hygroscopic, decomp. in moist air, dissolves in a few min. in boiling  $\text{H}_2\text{O}$ , mol. wt. in freezing  $\text{AcOH}$  215-42. *Iso-ox-ozonide*, from the diene in  $\text{AcOH}$  treated 48 hrs. with  $\text{O}_3$ , powder, m.  $105-8^\circ$ , explodes at higher temps., is less hygroscopic than IX but dissolves easily in  $\text{H}_2\text{O}$ . *Polydicyclopentadiene diozonide*, amorphous, sinters  $114^\circ$ , m.  $120-5^\circ$  (decompn.), is more explosive than IX, dissolves in boiling  $\text{AcOH}$  with decompn., decomp. on long boiling with  $\text{H}_2\text{O}$  (much resinification), changes on long standing, becoming sol. in  $\text{Me}_2\text{CO}$  and in hot  $\text{H}_2\text{O}$  without resin formation. *Polydihydrodicyclopentadiene ozonide*, from XI and  $\text{O}_3$  in  $\text{CCl}_4$ , explosive powder, m.  $125-$

30°, sol colloiddally in  $C_6H_6$ ,  $CCl_4$  and  $CS_2$ , very difficultly decompd. by  $H_2O$ , sol. in boiling  $AcOH$  with decompn. mol. wt. in  $C_6H_6$ , 3840-6250. No ozonide can be obtained from XI in  $AcOH$  C. A. R.

Semicarbazones of benzoin. I. I. V. HOPPER. *J. Chem. Soc.* 127, 1282-8 (1925).— $BzCH(OH)Ph$  in  $C_6H_5N$  gives a mixt. of 2 semicarbazones, the  $\alpha$ -form, m. 205-6° (Bultz. *Ann.* 339, 243 (1905)), and the  $\beta$ -form, m. 186-7° (decompn.), mol. wt. in boiling  $EtOH$  279, which is found in the mother liquors of the  $EtOH$  used for crystn. Hydrolysis of either form gives  $BzCH(OH)Ph$ .  $BzCH(OH)Ph$  and  $H_2NNHCONHCH_2Ph$  gave a mixt. of benzil di- $\delta$ -benzylsemicarbazone (I), benzil mono- $\delta$ -benzylsemicarbazone, m. 198°, and some  $BzCH(OH)Ph$ . From larger amts. of  $EtOH$ , there results I and benzoin  $\delta$ -benzylsemicarbazone, m. 115°. Benzoin  $\delta$ -phenylsemicarbazone,  $\alpha$ -form, m. 198° (decompn.), results when  $EtOH$  is used as a solvent, and also in  $C_6H_5N$ , when the  $\beta$ -form, m. 169°, also results (With MAGNUS HERD). Benzil di- $\delta$ -phenylsemicarbazone, m. 253° (decompn.), in 70% yields  $\delta$ ,  $\alpha$ -Phenylethylsemicarbazone,  $\alpha$ -form, m. 174°,  $\beta$ -form m. 154°,  $\gamma$ -form m. 137°. C. J. WEST

$\alpha$ -Phenylacetylidesoxybenzoin, its conversion into substituted naphthalenes and an attempt to prepare other  $\alpha$ -phenylene derivatives. RICHARD WEISS and LIZZIE SOVENSCHTEIN. *Ber.* 58B, 1043-7 (1925).—Isobenzaldehyde (23 g.) with  $PhCH_2MgCl$  yields 18 g.  $\alpha$ -phenylacetylidesoxybenzoin,  $PhCH_2COC_6H_4CH_2COPh$  (I), m. 146-50°; often, on acidifying the reaction mixt. with  $HCl$ , there seps, at once a small amt. of a solid acid, begins to soften 170°, does not m. completely 250°. With  $Na$  in abs.  $EtOH$  in the ice chest, 6 g. I gives 5.5 g. crude or 4.9 g. pure 2,3-diphenyl-1-naphthol, m. 128-31°; acetate, m. 161-3°, sapond. back to the naphthol by 5% alc.  $KOH$ . With  $Na_2Cr_2O_7$  in boiling  $AcOH$  6 g. of the naphthol gives 2.1 g. 2,3-diphenyl- $\alpha$ -naphthoquinone, yellow, m. 140-2°. Allowed to stand several days with  $Na$  and  $AmONO$  in alc. in a closed vessel in the cold, 10 g. I yields 9.7 g. 3-phenyl-1-benzoyl-4-hydroxyisoquinoline (II), yellow, m. 193° (decompn.), acetate, crystals with 0.5  $H_2O$ , m. 138-41°, sapond. back to II by boiling 5% alc.  $KOH$ . With  $AmONO$  on the  $H_2O$  bath II gives 2,6-dibenzoyl-3,4-benzofuran, dark red, m. 233-4° (decompn.), converted by boiling 5% alc.  $KOH$  into  $\alpha$ -phenylenedi-phenyldiglycolic acid monolactone,  $C_6H_4CPh(OH)COO.CPhCO_2H$ , yellow-green crystals with 0.5  $H_2O$ , m. 206-7° (decompn.), turned green by concd.  $H_2SO_4$ ; mono- $Me$  ester, prepd. with  $CH_3N_3$ , light yellow, m. 204-6°. C. A. R.

The nitration and constitution of naphthalene. CRUSEPPEN ODNO. *Gazz. chim. ital.* 55, 174-184 (1925).—The only known practical method of obtaining a  $C_{10}H_7NO_2$  (I) is by the electrolysis of a mixt. of dil.  $HNO_3$  +  $C_{10}H_8$  (II), although it is an important source of synthetic dyes. O. noticed that when II is placed in  $HNO_3-H_2SO_4$  the temp. begins to rise, at 35° II begins to melt and a yellowish oil is formed; the temp. continues to rise to 55-6°. If the temp. is kept at 45-50° during the addn. of II and the mixt. is agitated afterwards at the same temp. the yellow oil crystals, giving pure I quant. Prolonged action is harmful. The procedure described has been applied industrially for the economical and rapid prepn. of pure I. By analysis it was found that the oil loses

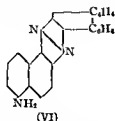


1 mol.  $H_2O$  for each mol. of I during the coagulation which indicates that nitration takes place by the formation of an oily addn. product of  $HNO_3$  with II which then gives I by the elimination of  $H_2O$ . This addn. which occurs so easily with aromatic compds, resembles that of the aliphatic ethylene compds and gives an interesting indication as to the constitution. Of the formulas proposed for II (Erlenmeyer (1866), Berthelot (1866), Wieden Claus (1876), Bamberger (1890), Armstrong (1890), Thiele (1899), Aldo (1906)) O. prefers his own for the interpretation of this reaction, because it represents I as constituted of a truly aromatic hexagonal ring while the rest of the mol. has an aliphatic structure confg. 2 so-called conjugated double bonds. Accordingly the only addn. product is III and I is IV. The formation of 1,2,3-nitrophthalic acid by oxidation

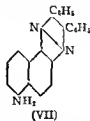
and the formation of 1,5- and 1,8- $C_{10}H_6(NO_2)_2$  (V and VI) indicates that the benzenic character is transferred to the substituted ring and that  $HNO_3$  now adds, giving VII and its isomer, and these, by the loss of  $H_2O$ , give V and VI, resp. It was found that with  $HNO_3$  I gives both at  $40^\circ$  and  $65^\circ$  an oil having the compn.  $C_{12}H_4(NO_2)_2 \cdot 3H_2O$ , which loses 3 mol.  $H_2O$  *in vacuo*, giving a mixt. of V and VI. Both  $NO_2$  groups combine with  $H_2O$  giving  $-N(O)(OH)_2$ . In the industrial prepn. of I 128 g. II is added to a mixt. of 75 l.  $H_2O$  + 150 kg.  $HNO_3$  ( $40^\circ$  B $\acute{e}$ ) + 275 kg.  $H_2SO_4$  (66 B $\acute{e}$ ). The kettle is equipped with a good agitator, a thermometer and a cover and placed in a  $H_2O$  bath so that the temp. can be kept at  $45-50^\circ$ . The addn. of I requires 1-2 hrs.; about 0.5 hr. later the oil first formed begins to crystallize and the reaction is over. The acid is siphoned off, the product is washed twice with  $H_2O$  and worked up in a suitable form. Another formula for the prepn. of I that is more convenient for the continuous manufacture of I is given.

E. J. WITZEMANN

**Dinitro- and triaminonaphthalenes.** C. FINZI. *Ann. chim. applicata* 15, 55-62 (1925).—The method of Friedlander (*Ber.* 32, 3531 (1899)) for prepn. 1,5- $C_{10}H_6(NO_2)_2$  (I) does not allow a good sep'n. of I and its 1,8-isomer (II). Much better results can be had by the following procedure. Dissolve  $\alpha$ - $C_{10}H_7NO_2$  (150 g.) in 95-6%  $H_2SO_4$  (1800 g.) at  $10^\circ$ , nitrate with 350 g. of a mixt. contg. 88.63%  $H_2SO_4$ , 5.97%  $HNO_3$ , and 5.40%  $H_2O$ , keeping the temp. at  $20-5^\circ$ , heat to  $90^\circ$  to dissolve any ppt., cool slowly to  $50^\circ$ , let stand, filter off I through asbestos, keeping it at  $50^\circ$ . The yield of I, which is almost pure (m.  $204-6^\circ$ ), is about 35 g. On cooling the filtrate to  $30^\circ$ , there seps. about 30 g. of a mixt. of I and II, m.  $144-8^\circ$ , contg. about 25% I. On filtering at  $15^\circ$  there is obtained 40 g. more, m.  $145-50^\circ$  and contg. a small amt. of I. The acid recovered contains 91%  $H_2SO_4$  and can be used over again when fortified with oleum. *p*-Toluidine (107 g.) in  $H_2O$  contg. concd.  $HCl$  (25 g.) was diazotized at  $4-5^\circ$  with concd. aq.  $NaNO_2$  (7 g.), poured into  $H_2O$  contg. 1,5- $C_{10}H_6(NH_2 \cdot HCl)_2$  (23 g.) (III) and  $NaOAc$  (30 g.), keeping the temp.  $8-10^\circ$ , let stand several hrs., heated to  $70-80^\circ$ , cooled and the insol. blue-violet dye filtered and washed. This dye on reduction in hot alc.  $HCl$  with  $Sn$  gave a yellowish residue, 1,2,5-naphthalenetriamine chlorostannate,  $p$ - $MeC_6H_4NH_2 \cdot Cl$  remaining in soln. This double salt was insol. in concd.  $HCl$  and  $HOAc$  and gave white needles when pptd. from hot  $H_2O$  by  $HCl$ . Treatment of its aq. soln. with  $H_2S$  pptd.  $SnS$  and on filtration, concn. to 0.5 the vol., decolorization with animal charcoal, final concn. in a current of  $H_2$ , addn. of an equal vol. of concd.  $HCl$  and letting stand out of contact with air gave 1,2,5-naphthalenetriamine- $HCl$  (IV), white tufted crystals, turning brown rapidly in  $H_2O$  and blackening almost instantly when made alk., gives a blue-violet color with  $HCl$  and  $FeCl_3$ . Treated by the method of Schotten and Baumann with  $BzCl$  it gave the *tri-Bz* deriv.,  $C_{10}H_6(NHBz)_3$ , yellowish, m.  $268^\circ$ . It does not crystallize from any ordinary solvent and must be purified by repeated washing with glacial  $HOAc$ , in which it is insol. Pbenanthrenequinone (15 g.) (V) and  $NaOAc$  (25 g.) in concd.  $HOAc$  shaken with a suspension of IV (2 g.) in 96%  $EtOH$ , filtered, washed successively with boiling concd.  $HOAc$ ,  $H_2O$ , dil. aq.  $Na_2CO_3$ , and finally  $H_2O$  gives 7-amino-2,3-diphenylnaphthoquinoxaline (VI), greenish, does not m. up to  $300^\circ$ , gives an intense blue soln. in concd.  $H_2SO_4$  and a red soln. in concd.  $HCl$  and heated with alc.  $KOH$  and  $CHCl_3$  it gives an isonitrile odor. It is insol. in all ordinary solvents and can be obtained in a pure form only by starting with pure compds. Equimol. wts. of alc. IV and benzil boiled for some time with  $NaOAc$ , filtered and washed with boiling



(VI)



(VII)

$EtOH$ , gives on crystn. from concd.  $HOAc$  7-amino-2,3-diphenylnaphthoquinoxaline (VII), yellow, m.  $208^\circ$ , gives a bright red color with concd.  $H_2SO_4$ . Following the procedure for prepn. IV the product was resinous and was easily oxidized by the air. The best results were obtained by prepn. 3 solns. (1) *p*-toluidine (107 g.) in  $H_2O$  contg.  $HCl$  (25 g.) diazotized with  $NaNO_2$  (7 g.); (2) aq.  $NaOAc$  (30 g.) and (3) concd. aq. 1,8- $C_{10}H_6(NH_2 \cdot HCl)_2$  (VIII) (23 g.) and adding (1) and (2) simultaneously to (3), shaking and keeping below  $10^\circ$ . The mixt. was then let stand, heated to  $70-80^\circ$ , the

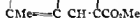


yellow, m. 245°. 2-Carboxy 4,5-methylenedioxyphenylacetonitrile, m. 195–6°; 4,5-methylenedioxyhomophthalamic acid, softens 230°, darkens 280° and m. 295°, which is the m. p. of the corresponding homophthalimide C. J. WEST

Reduction of the bromoanthraquinones. E. DE B. BARNETT AND J. W. COOK. *J. Chem. Soc.* 127, 1489–90 (1925).—Attempts to prep 1- and 2-bromo- and 2,3-dibromoanthracene by the reduction of the corresponding quinones have shown that in each case the Br is lost and only anthracene is isolated. 9,10-Dibromoanthracene tetrahydride in cold  $C_4H_{10}N$  loses both Br and HBr and the resulting 2,9,10-tri- and 2,3,9,10-tetrabromoanthracenes may be sep'd by fractional crystn. from AmOH.

C. J. WEST

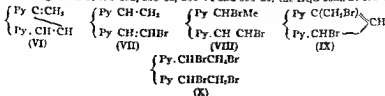
3,5-Dimethyl-4-carbethoxypyrrole-2-[vinyl- $\omega,\omega$ -dicarboxylic acid] and 2-[vinyl- $\omega$ -carboxylic acid]. WILLIAM KÜSTER, ERNST BRUDI AND G. KOPPENHÖFER. *Ber.* 58B, 1014–21 (1925).—As long as the presence of 2 vinyl groups on 2 of the pyrrole nuclei in the hemin mol. was considered probable it did not seem devoid of interest to study the addn. of halogens or halogen acids to less complex, monocyclic pyrrole derivs. having a vinyl group as a side chain 2-Vinyl-3,5-dimethyl-4-carbethoxypyrrole (I), which was first chosen, must, however, be an exceedingly labile substance which cannot easily be obtained in pure state. Its  $CO_2H$  derivs, 3,5-dimethyl-4-carbethoxypyrrole-2-[vinyl- $\omega$ -carboxylic acid] (II) and 2-[vinyl  $\omega,\omega$ -dicarboxylic acid] (III), were therefore selected next. They are formed together by the condensation of 2-formyl-3,5-dimethyl-4-carbethoxypyrrole (IV) with malonic acid under the influence of alc.  $NH_3$  and are sep'd. through their K salts, that of II being wholly insol., that of III somewhat sol. in alc. Probably the  $CH_2(CO_2H)_2$  condenses in the form of the acid  $NH_4$  salt so that there is only a partial splitting off of  $CO_2$ , that this is not complete is probably due to the N of the pyrrole coming into relation with the 2nd  $CO_2H$  group, for when III is boiled a long time (60 hrs.) in abs. MeOH there is an intramol. elimination of  $H_2O$  with formation of the mono-Me ester anhydride,  $EtO_2CC$  CMe N—CO (V). On long boiling



of III in EtOH, however, there is no such loss of  $H_2O$ , yet the resulting mono-Et ester (VI) shows no acid properties and therefore probably has a betaine-like structure. On the other hand, the mono-Et ester (VII) obtained from the mono-Ag salt with EtBr, although having the same compn., has properties entirely different from those of VI and also from those of the mono-Me ester (VIII) obtained from the Ag salt and MeI. VIII smoothly loses  $CO_2$  a few degrees above its m. p. and yields the ester of II (which can also be obtained from the Ag salt of II while the other usual methods of esterification fail completely; thus, with MeOH-HCl, resinification occurs even at room temp.), while VII loses  $CO_2$  only 60° above its m. p. and simultaneously undergoes further decompn. Again, VIII in  $C_4H_8$  with  $NH_3$  at once gives a ppt. of its  $NH_4$  salt while VII yields only a slight turbidity after 6 hrs. Both VII and VIII have, to be sure, the same canary-yellow color, are sol. in 96% alc. only on heating and sep. in slender needles, but only those of VII have a tendency to form a felted mat which can be lifted up with tweezers. For the prepn. of III in quantity it is best to use  $NH_4Et$  and  $CH_2(CO_2H)_2$  in boiling alc. (yield, 102% of the IV used). Attempts to prep. I by heating II above its m. p. led to complete decompn. even *in vacuo*. III at 205° melts with vigorous evolution of  $CO_2$  and development of the typical odor of dimethylpyrrole and there remains a dark gray glassy mass insol. in alkalis and easily sol. in alc. and  $Me_2CO$  but sepp. again only as a red-brown resin; similar results are obtained on heating *in vacuo*. With HBr-AcOH, III loses  $CO_2$  and changes into II, while II is resinified by HBr-AcOH. In a Br atm., however, II becomes deep violet in a few hrs., and when the excess of Br is removed *in vacuo* there remains impure 3,5-dimethyl-4-carbethoxypyrrole-2-[ $\alpha,\omega$ -dibromoethyl- $\omega$ -carboxylic acid] (IX), which rapidly loses HBr; at 82° this loss seems to amount to 1 mol. but as the residue does not m. 300° several mols. are probably involved in the loss of HBr. The ester of III behaves in the same way with Br in  $CHCl_3$ . With I in  $Et_2O$  in bright sunlight, the di-Et ester of III gives di-Et 3,5-dimethyl-4-carbethoxypyrrole-2-[ $\alpha,\omega$ -diiodoethyl- $\omega,\omega$ -dicarboxylate] (X); the I is completely removed in  $Et_2O$  by  $Na_2S_2O_8$  and boiling in alc. apparently replaces it by EtO. III is smoothly reduced by Na-Hg, although the reduced acid has not yet been obtained entirely colorless and in well crystd. form; the faintly greenish needles m. 232° (Maurer, C. A. 18, 1493, gives 218°) with vigorous gas evolution and formation of the propionic acid but only in 28% yield; the latter is therefore best prepd. (90% yield) by direct reduction of II with alk. Na-Hg. II, green-yellow amorphous substance, m. around 265°; Ag salt, green-yellow curdy ppt.; Me ester, from the Ag salt and MeI refluxed in xylene, needles with yellow-orange tinge, m. 179–81°; Et ester, m. 155–7°. III, light green, m. 199–200°, loses

$\text{CO}_2$  at  $202^\circ$ , mol wt in camphor 288-97, *di-Ag salt*, green-yellow flocculent ppt.; *di-Et ester* golden yellow, from the Ag salt and EtBr in boiling  $\text{C}_6\text{H}_6$ , m.  $86-7^\circ$ , also obtained in 92% yield from IV,  $\text{CH}_2(\text{CO}_2\text{Et})_2$  and  $\text{NH}_4\text{Et}_3$  heated 1 day in alc.; the yellow soln. with brownish tinge of the *di-Na salt* gives with alk. earth salts yellowish brown, with  $\text{ZnSO}_4$  and  $\text{Cd}(\text{OAc})_2$  yellow, with  $\text{CuSO}_4$  green-yellow, with  $\text{NiSO}_4$  light green flocculent ppts. *Mono Ag salt*, green-yellow ppt. VII, m.  $114^\circ$ , decomps. completely  $174^\circ$ . VIII, m.  $161^\circ$ , decomps. completely  $163^\circ$ . VI, yellow, m.  $183^\circ$ , does not evolve  $\text{CO}_2$  even at  $280^\circ$ , mol wt in camphor 313.9. V, yellow-green, does not melt but darkens  $260^\circ$ , has no acid properties, mol wt in camphor 278.06. X (yield, 47.1%), amber-yellow m.  $175^\circ$ . C. A. R.

The prosthetic group of the blood pigment. WILLIAM KÜSTER AND WALTER HIGGS. *Ber* 58B, 1022-7 (1925), cf. C. A. 18, 2893, and earlier papers—K. had assumed that the 1st pair of unsatd. positions in the heminmol. (I) is made up of 4 methine groups joining through the  $\alpha$  positions 4  $\beta$ -substituted pyrrole nuclei, and that the 2nd pair of unsubstituted positions consists of 2 vinyl groups as  $\beta$ -side chains of 2 of the pyrrole rings. Willstätter and H. Fischer, on the contrary, believe that the 4 pyrrole nuclei are joined by a C-C bridge. With Br in  $\text{CHCl}_3$  chloro- or bromohemin yields chiefly a dibromide; if W.'s views were correct and the Br adds at the C-C bridge, the dye character of the I should be materially altered, for in his formulation it is this bridge solely which is the chromophore. As a matter of fact, however, the absorption spectrum of dimethyl(bromo)hemin (II) shows a strong band at  $620-40$  and weak bands at  $535-55$  and  $500-20$  and its dibromide (III) a strong band at  $618-35$  and weak bands at  $535-50$  and  $500-13$ . It may therefore be concluded that the Br does not add at the unsatd. positions which condition the dye character. Neither, however, can it have added at a "vinyl" group, for in such a case the dibromide would no longer be capable of complete hematoporphyrin formation; actually, however, III freed from Fe with HBr-AcOH and subsequently treated with MeOH yields *dibromohematoporphyrin dimethyl ether* (IV), i. e., the added Br remains in the mol and yet 2 mols. HBr have been further added. Oxidation of IV yields a brominated imide  $\text{C}_{37}\text{H}_{36}\text{O}_8\text{NBr}$  (V), which in all probability is *methyl[ $\beta$ -bromo- $\alpha$ -methoxyethyl]maleimide*. The yield of V per mol of IV is 2 mols., together with 2 mols. hematinic acid. All 4 pyrrole nuclei of the prosthetic group of the pigment have thus far for the 1st time been accounted for in an oxidation reaction and it has further been established that the addn. of Br occurs at 2  $\beta$  side chains which must be joined to each other in I and which can no longer be assumed to consist of 2 vinyl groups ( $\text{C}_2\text{H}_5$ ) but must contain 2 atoms less of H ( $\text{C}_2\text{H}_3$ ), for 2 mols. of HBr must still be added before porphyrin formation occurs. Of the possible structures for the group  $\text{C}_2\text{H}_3$ , preference is given in VI; addn. of HBr alone would lead through VII to VIII; addn. of Br to the ester in  $\text{CHCl}_3$  would give IX and further addn. of HBr X. II, prepd. from the Cl deriv. in  $\text{CHCl}_3$  with 66% HBr and recrystd. from AcOH, is insol in MeOH but sol in MeOH acidified with dil.  $\text{H}_2\text{SO}_4$ , insol. in hot 5%  $\text{Na}_2\text{CO}_3$  and gives off practically no Br in  $\text{Na}_2\text{CO}_3$  at room temp. (the difference in behavior towards  $\text{Na}_2\text{CO}_3$  of the II described in the earlier paper is probably due to the fact that the latter was prepd. from the Cl deriv. in  $\text{CHCl}_3$  in the presence of  $\text{C}_6\text{H}_5\text{N}$ ). When III is boiled 3 hrs. in MeOH, approx. 1 Br atom is replaced by MeO. IV has an acid no. of 5.7 (non-brominated ether, 4.5), is sol in  $\text{NaHCO}_3$ , gives in  $\text{Et}_2\text{O}$  with  $\text{NH}_3$  or HCl orange red or red violet ppts., resp., which quickly lose again the added  $\text{NH}_3$  or HCl; the spectrum of the HCl soln. has 2 sharp bands at  $548-82$  and  $588-92$ , the  $\text{CHCl}_3$  soln. 4 strong bands at  $492-512$ ,  $528-38$ ,  $560-74$  and  $605-20$ , the  $\text{Et}_2\text{O}$  soln. at  $494-505$ ,



$525-34$ ,  $563-70$  and  $605-20$ , esterification with 1% HCl in boiling MeOH gives an alkali-insol., optically inactive substance, sinters  $87^\circ$ , m.  $147^\circ$  (foaming). V, m.  $75^\circ$ , mol wt. in boiling  $\text{CHCl}_3$  226. C. A. R.

A synthesis of *N*-aryl- $\alpha$ -pyrroldiones. P. LIPP AND F. CASPERS. *Ber* 58B, 1011-4 (1925).  $\gamma$ -Chlorobutyramide (I) and the *p*-toluidide (II) fused a short time with alkalis under definite conditions lose HCl and smoothly yield *N*-phenyl- (III) and *N*-

*p*-tolyl- $\alpha$ -pyrrolidone (IV), resp. III and IV are only very weakly basic, their solns in concd. mineral acids are completely hydrolyzed on diln with  $H_2O$ , they are unchanged by short boiling with dil  $H_2SO_4$  or alkalis. In prepg the  $Cl(CH_2)_3CO_2H$  from the nitrile by Cloves' method (Ann 319, 360 (1901)) it is not necessary to follow his tedious process of purification, as a single distn in a high vacuum yields the pure acid,  $b_p$  93.5–4.0°,  $m$  15–6°. The chloride, prepd with  $SOCl_2$  in petroleum ether,  $b_p$  59–60°. I,  $m$  69–70° (all  $m$  vs are cor.), darkens on standing. II,  $m$  91–2.5°, also darkens on long standing (2 years). III, from I heated with 3 parts powd KOH to incipient fusion (about 0.5 mm)  $m$  68–9°. IV,  $m$  88–9°, *picrate*, deep orange,  $m$ . 121–2°.

C A R

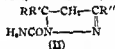
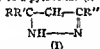
**6,7-Hydroxycoumarone compounds.** K. FRIES AND M. NOHREN *Ber* 58B, 1027–34 (1925); cf. Sonn and Patzschke, *C A* 19, 1421. — The assumption that the usual methods for the prepn of simple coumarones are "not at all or only ill adapted" to the prepn. of HO derivs is too sweeping. Thus, 3-methyl-6-hydroxycoumarone (I) is obtained most easily and in best yield by the Fittig-Ebert method. To avoid substitution in the nucleus in the bromination of the 4-methylumbelliferone (II), the *Et* carbonate (III) is used instead of the II itself. The resulting 4-methyl-7-hydroxy-3-bromocoumarin *Et* carbonate (IV) yields I directly in 80% yield when boiled with  $Na_2CO_3$ . 6-Hydroxy-3-methyl-2-coumaric acid (V) is certainly not an intermediate product, as it is unchanged by boiling  $Na_2CO_3$ . From the deep blue soln of I in  $Et_2O-HClO_4$  there seps, a colored cryst. compd  $C_{11}H_{10}O_4$ ,  $HClO_4$  (VI), and  $HCl$  yields a similar substance. These blue compds have a salt like character and are stable towards reducing agents; they cannot be converted back into I. With Cl or Br in mol amts I yields blue-black compds,  $C_{11}H_{10}O_4X$  (VII), in which the halogen is replaced by H on mere boiling in  $Me_2CO$ ; the resulting colorless compd  $C_{11}H_{12}O_4$  (VIII) forms di-Me and di-Ac derivs and is doubtless a deriv of a dicoumarone, Cl or Br convert it back into the VII; with  $FeCl_3$  it forms a deep blue, indigo-like substance (IX),  $(C_{11}H_{10}O_4)_2O$ , unchanged by  $SnCl_4$ . 4-Methyl-7-hydroxycoumarin *Et* carbonate (III), obtained in 95% yield from II in 1 equiv. 2  $N$  NaOH with 1 equiv.  $ClCO_2Et$ ,  $m$  102°. IV (85% from III and 1 mol  $Br_2$  in  $CHCl_3$ ),  $m$  144°, gives in alc. with dil.  $NH_4OH$  and subsequent acidification the free HO compd,  $m$  215°, dissolves in concd.  $H_2SO_4$  with blue fluorescence, forms yellow alkali salts whose dil. solns. show blue-green fluorescence. V, from IV rubbed to a paste with alc. and boiled with 5 parts of 50% KOH,  $m$  226°, sol in concd.  $H_2SO_4$  without color but becoming red-violet on heating, the solns. of its salts show blue fluorescence, the *Et* carbonate,  $m$  189°. I,  $m$ . 103°, the AcOH soln contg a few drops  $H_2SO_4$  gives with  $K_2Cr_2O_7$  or  $H_2O_2$  a dark blue ppt. which soon disappears again, and in alk. soln.  $K_3Fe(CN)_6$  forms a blue-green ppt. which also quickly disappears. *Et* carbonate of I,  $m$  54°, sol. in concd.  $H_2SO_4$  with yellow color and strong green fluorescence, the soln. gradually becoming red and then violet. Benzoate,  $m$  102°. VI (yield, generally 0.1 g. from 3 g. I), green needles with metallic luster, blackens 125°, does not  $m$  450°, cannot be recrystd., sol. in AcOH with blue, in alc. with red-violet, in concd.  $H_2SO_4$  with deep blue color (violet on long standing), in dil. NaOH with deep blue color which soon disappears although acids reppt. blue flocks, acetylation and benzylation give colorless amorphous products. Boiled in AcOH with  $HClO_4$ , I forms a blue-black cryst. mass differing from VI in being Cl-free and in its difficult soly. in the usual solvents. VII (X = Br), black,  $m$ . 218° (decompn.), decomp. both in the air and in a desiccator, dissolves slowly in dil. alkalis with decompn., liberates I from concd. KI under  $CHCl_3$ , dissolves in  $H_2SO_4$  with brown color changing to red and finally violet. VII (X = Cl), blue-black,  $m$ . around 190° (decompn.). VIII, begins to darken 240°,  $m$ . 254°, mol. wt. in boiling  $Et_2O$  289, obtained from VII with boiling  $Me_2CO$  or with  $SnCl_4$ -AcOH, quickly becomes blue in the light, shows strong blue fluorescence in dil. alkalis, is stable towards HBr and HCl; the AcOH soln. is colored red by  $HClO_4$ ;  $CrO_2$  produces a blue color which soon disappears again. Diacetate,  $m$  222°. Di-Me ether,  $m$  191°, mol. wt. in boiling  $C_6H_6$  314, is unchanged by  $FeCl_3$ . IX dissolves in AcOH with violet color changing to red on heating; when rubbed with a little NaOH and then treated with alc. the soln. shows at first a blue fluorescence which, however, soon disappears. 7-Hydroxycoumarin *Et* carbonate,  $m$  98°, cannot be brominated in  $CHCl_3$ , but in AcOH with NaOAc and a 50% excess of Br it gives 55% 7-hydroxy-3-bromocoumarin *Et* carbonate,  $m$  132°, sol. in  $H_2SO_4$  without color and, unlike the 4-Me homolog (IV), cannot be converted by boiling  $Na_2CO_3$  into the hydroxycoumarone, but when moistened with alc. and boiled with 50% KOH it gives 88% 6-hydroxy-2-coumaric acid, decomp. 264° (Karrer, Glattfelder and Widmer, *C A* 15, 368, give 234–6°). 7-Hydroxy-3-bromocoumarin, from the *Et* carbonate and boiling 10% NaOAc,  $m$  242° (decompn.), shows in alkalis yellow-green, in  $H_2SO_4$  blue fluorescence. 4-Methyl-6-hydroxycoumarin

*Et carbonate*, m. 134°, is unchanged by Br in AcOH or CHCl<sub>3</sub> after 3 days; after 6 hrs. at 100° in a sealed tube, the product contains 1% Br; with greater concns. of Br or at higher temps., substitution in the C<sub>6</sub>H<sub>5</sub> nucleus occurs. C. A. R.

A new indole synthesis. COSTIN NEMITZESCU. *Ber.* 58B, 1063-4 (1925).—Reduction of *o*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>NO<sub>2</sub> leads directly to the formation of indole (probably through H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>NOH as an intermediate product). The best yields (30%) are obtained with Fe filings and dil. AcOH, Zn gives poorer yields and Al-Hg only smears. Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> gives a good yield of indigo, doubtless formed secondarily from the indole by the action of the air. C. A. R.

The isolation of an amino acid of the indole series of the composition C<sub>11</sub>H<sub>11</sub>O<sub>2</sub>N<sub>2</sub> from casein. EMIL ABDERHALDEN AND HANS SICKEL. *Z. physiol. Chem.* 144, 80-4 (1925); cf. C. A. 18, 3188.—The substance isolated from the hydrolytic products of casein and provisionally considered an indole deriv. contains tyrosine and is probably a complex of tyrosine and proline contg. 2.5 mols. H<sub>2</sub>O, or a complex of tyrosine and  $\alpha$ -amino- $\delta$ -hydroxyvaleric acid contg. 1.5 mols. H<sub>2</sub>O. The complex appears to be characteristic of casein. A. W. DOX

New triazotized bases. Ureas of pyrazolines. R. LOCQUIN AND R. HEILMANN. *Compt. rend.* 180, 1757-60 (1925).—Several new pyrazolines were prepd. and from them their PhSO<sub>2</sub>H, *p*-BrC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H and HOCN derivs. to det. whether by means of these derivs. various pyrazolines can be distinguished. Furthermore no previous work has been published on the action of HOCN on pyrazolines. When a large excess of KOCN is added slowly to a pyrazoline (I) in cold AcOH, a urea deriv. (II) is obtained quant.



After 2 days the soln. is made alk. with concd. K<sub>2</sub>CO<sub>3</sub> and the urea is extd. with Et<sub>2</sub>O. The II are weak bases, are very stable at ordinary temp. and can be distd. *in vacuo* at 70-90° without decompn. They form picrates, dissolve in acids to form salts difficult to obtain pure, can be acylated, react with BrCl in C<sub>6</sub>H<sub>5</sub>N at 100° to form di-Bs derivs., do not react with 10% KOH or NaOH even after prolonged boiling, revert to the pyrazoline on boiling with dil. HCl and are decompd. by HNO<sub>3</sub> at 0°, forming the ketone corresponding to the original pyrazoline. The I are easily oxidized and had to be distd. *in vacuo* or in N. 3,5,5-Trimethylpyrazoline, from mesityl oxide, b<sub>10</sub> 51-2°, decompd. by HCl and NaNO<sub>2</sub> into mesityl oxide and N<sub>2</sub>CONH<sub>2</sub> (cf. *Ann.* 283, 38 (1894)). Urea deriv., m. 129°, b<sub>10</sub> 140-1°; picrate, m. 136-7°. 3-Methyl-5-isopropylpyrazoline, from isobutylidene acetone, b<sub>10</sub> 75-7°. Benzenesulfonate m. 109° (increases to 114° after oven drying). *p*-Bromobenzenesulfonate m. 134-5°. Urea, m. 116-7°, b<sub>10</sub> 155-7°; di-Bs deriv., m. 141°, reverts to the original pyrazoline when boiled with dil. HCl. 3-Methyl-5-isobutylpyrazoline, from isoamylidene acetone, b<sub>10</sub> 90-2°. Benzenesulfonate m. about 93° (increases to 115° after oven drying). Urea, m. 110-1°, b<sub>10</sub> 162-8°; di-Bs deriv., m. 128-9°. The urea reverts to its pyrazoline on boiling with 20% HCl. 4-Methyl-5-ethylpyrazoline, from EtCH:CMcCHO, b<sub>10</sub> 65-70°. Benzenesulfonate m. 118°. Urea, m. 100-10°, b<sub>10</sub> 155-60°. The pyrazoline ureas have the same % compn. as the normal semicarbazones of the ketones or non-satd.  $\alpha$ - or  $\beta$ -aldehydes from which the pyrazolines were prepd., i. e., the 2 groups of compds. are isomeric. This is of particular significance with the urea derived from mesityl oxide, for the former is identical with the base C<sub>7</sub>H<sub>11</sub>ON<sub>2</sub> formed during the reaction of semicarbazide with mesityl oxide (cf. *Ber.* 29, 610 (1896); 37, 1338 (1899)), the compn. of which has never been heretofore explained (cf. Rupe and Kessler, C. A. 4, 590). C. C. DAVIS

Bromination of 4'-amino-1-phenyl-5-methylbenzothiazole and of 1,1-bisbenzothiazole. R. F. HUNTER. *J. Chem. Soc.* 127, 1318-20 (1925).—Dehydrothiolumidine in CHCl<sub>3</sub> gives quant. the dark red dibromide, m. 190°; it cannot be diazotized, HNO<sub>3</sub> causing the evolution of Br and production of resins; it lacks the explosive properties usually associated with the group :NBr, is relatively stable in air, boiling H<sub>2</sub>O and dil. alkalis and is reconverted by H<sub>2</sub>SO<sub>4</sub> or NaHSO<sub>4</sub> into dehydrothiolumidine; it is prob-

ably a perbromide of the formula  $\text{MeC}_6\text{H}_4 \begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ \text{NBr}_2 \end{array} \text{CC}_6\text{H}_4\text{NH}_2$ . Bisbenzothiazole yields

a red-brown tetrabromide, which becomes pale yellow and loses Br at 170° but does not m. 300°; it loses Br on exposure to the air or in boiling EtOH contg. a trace of alkali and is reduced to the parent compd. by H<sub>2</sub>SO<sub>4</sub>. C. J. WEST

Chlorobenzothiazole dibromide. R. F. HUNTER. *J. Chem. Soc.* 127, 1488-9

(1925).—1-Chlorobenzothiazole (I) in  $\text{CHCl}_3$  with Br gives an orange-red dibromide, m. 139°. It loses Br on exposure to the air or on treatment with  $\text{H}_2\text{SO}_4$ , regenerating I. The Br atoms are therefore attached to the N. The action of Na upon I did not give 1,1-bisbenzothiazole.

C. J. WEST

2,4,5-Triphenyloxazole or benzilam. J. TRÖGER AND O. PHILIPPSON. *J. prakt. Chem.* 110, 65-85 (1925).—Repeated nitration of benzilam or imabenzil yields a trinitro deriv. (trinitrotriphenyloxazole) (I), yellow, m. 294°; the products of Laurent (*J. prakt. Chem.* 35, 461 (1845)) and of Henius (*Ann.* 228, 339 (1855)) were probably mists. of this with the di- $\text{NO}_2$  deriv I is only slightly attacked by concd. HCl in a sealed tube at 245°, by hot 30% KOH or by cold concd.  $\text{H}_2\text{SO}_4$ . I is not reduced by Sn and HCl; a very concd. HCl- $\text{SnCl}_2$  soln. did not give any large amt. of reduction product; the best reducing agent is Zn dust in AcOH-HCl, but only slimy ppts. were isolated, from which no pure salts could be prepd. No positive results were obtained by heating with EtOH- $\text{NH}_3$  under pressure.  $\text{CrO}_3$  gave only  $\text{NH}_3$  and  $p\text{-O}_2\text{NC}_6\text{H}_4\text{CO}_2\text{H}$ . By nitrating with  $\text{HNO}_3$  (d. 1.46) at 15° and pouring into  $\text{H}_2\text{O}$ , there results a mononitro deriv., yellow, m. 194°. This is decompd. by concd. HCl at 245°, giving  $p\text{-O}_2\text{NC}_6\text{H}_4\text{CO}_2\text{H}$ ; it is pptd. unchanged from concd.  $\text{H}_2\text{SO}_4$ .  $\text{CrO}_3$  in AcOH gives BrOH and  $p\text{-O}_2\text{NC}_6\text{H}_4\text{CO}_2\text{H}$ . Concd. EtOH-KOH gives an azoxybenzilam, brown, amorphous ppt., m. 270°; it could not be further reduced. Reduction with Zn dust in AcOH-HCl gives the amino deriv. (II), flesh-colored, m. 214°, the Et<sub>2</sub>O soln. has a marked fluorescence, EtOH solns. less so. Cryst. acid salts could not be obtained. chloroplatinate, yellow; chlorosaurate, yellowish green. Methiodide m. 171°; there also results a compd.,  $\text{C}_{20}\text{H}_{15}\text{N}_3\text{OI}$ , which may be a methiodide of a dimethylaminobenzilam.  $\text{Ag}_2\text{O}$  in EtOH transforms the methiodide into a base,  $\text{C}_{20}\text{H}_{15}\text{N}_3\text{O}$ , analyzed as the chloroplatinate, orange-red, m. 240°.  $\text{PhCH}_2\text{Cl}$  and II give the dibenzyl compd., reddish white, m. 182°. Benzilamazo- $\beta$ -naphthol, red amorphous product. If the diazo compd. is heated to 80°, there results hydroxybenzilam, yellow-brown, amorphous, m. 205°. The behavior of the diazo soln. with  $\text{SO}_2$  is discussed.

C. J. WEST

Acyclic  $\delta$ -diketones. Transformation to derivatives of pyridine. E. E. BLAISE AND M. MONTAGNE. *Compt. rend.* 180, 1760-2 (1925); cf. C. A. 19, 2478. Since in general simple acyclic  $\delta$ -diketones tend to form with  $\text{NH}_3$  a cyclenone, e. g., methylcyclohexenone from  $\text{EtCO}(\text{CH}_2)_3\text{COEt}$ , whereas more complex  $\delta$ -diketones form dihydropyridine derivs. (cf. *Ber.* 18, 2385 (1885); 20, 2756 (1887); *Ann.* 231, 69 (1885); 281, 95 (1894)), it follows that the latter diketones contain electronegative groups which favor enolization.  $\delta$ -Diketones may also be transformed to pyridine derivs. by  $\text{NH}_3\text{OH}$ , but according to Knoevenagel (*Ann.* 281, 34 (1894)) this method is applicable only when R and R' in the compd.  $\text{RCO}(\text{CH}_2)_n\text{COR'}$  are aryl, cyclohexenones being formed if they are alkyl (cf. *Ann.* 302, 235, 241 (1898)). This is incorrect, for dialkylated  $\delta$ -diketones can be transformed to pyridine bases by  $\text{NH}_3\text{OH}$ . Thus if  $\text{EtCO}(\text{CH}_2)_3\text{COEt}$  is heated in a sealed tube with excess  $\text{NH}_3\text{OH}$  HCl in dil. EtOH at 115-80°, tarry products are obtained, but if the mixt. is refluxed 6 hrs., 2 products are formed: (1) methylethylcyclohexenone oxime, m. 180°, and (2)  $\alpha,\alpha'$ -diethylpyridine, liquid with  $\text{C}_6\text{H}_5\text{N}$  odor, b.p. 71-3°; picrate m. 115°; chlorosaurate,  $\text{C}_{10}\text{H}_{13}\text{N}$  HCl  $\text{AuCl}_4$  m. 92°; chloroplatinate,  $(\text{C}_{10}\text{H}_{13}\text{N}.\text{HCl})_2\text{PtCl}_6$  m. 211-2°; methiodide m. 142°. If the diketone is first converted to the diaxime, m. 53-4°, and this is boiled with HCl in abs. EtOH, 60% of pyridine deriv. is obtained, with a small amt. of methylethylcyclohexenone oxime. The results indicate that  $\text{NH}_3\text{OH}$  will serve as a general means of prepd. pyridine derivs. from  $\delta$ -diketones, though the mechanism of the reaction is still obscure. C. C. D.

A modification of the Hofmann reaction occurring in the rupture of heterocyclic compounds. P. PETRENKO-KRITCHENKO AND V. BUTAI DE KATZMAN. *J. Russ. Phys. Chem. Soc.* 55, 397-402 (1924).—In contradistinction to the yellow, unsatd. open-chain compd. PhCH:CHCOCH<sub>2</sub>CHPhNHPh obtained by P.-K. and Malakhov (cf. C. A. 17, 3507) an isomer was prepd. which, being colorless, apparently is satd. Attribution of it to a cyclic formula seems to be justified; the compd. is probably triphenylpiperidone (I); lack of material prohibited a proof of the formula by various means. With Br in  $\text{C}_6\text{H}_6$  it forms a tri-Br deriv., accompanied by partial decompn. to  $\text{BrC}_6\text{H}_4\text{NH}_2$  (II). II having been removed with  $\text{H}_2\text{O}$  from the ppt. formed, the residue, tribromotriphenylpiperidone-HBr (III), was converted with dil.  $\text{Na}_2\text{CO}_3$  into the free base  $\text{C}_{21}\text{H}_{15}\text{Br}_2\text{NO}$  (IV), m. 148°. The Br content of the HBr salt does not correspond to normal compn. (2% off). Refluxing IV in  $\text{CHCl}_3$  for 20 hrs. causes evolution of  $\text{Br}_2$  and pptn. of  $p\text{-BrC}_6\text{H}_4\text{NH}_2$ -HBr (V). The filtrate from V on evapn. gave a residue, m. 145-51°, presumably of PhCH:CHCOCHBrCHBrPh (VI). Br with VI in  $\text{CHCl}_3$  gave quant.  $\text{CO}(\text{CHBrCHBrPh})_2$ , m. 210°.

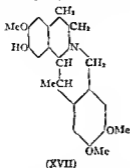
H. BERNHARD

Preparation and properties of organic chlorostannites and chlorostannates. VII.

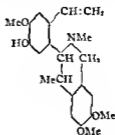


$C_6H_5CH_2Cl$  in PhMe for 24 hrs, reducing the ammonium bromide with Sn and HCl and decomp. the Sn salt with  $H_2S$ , the amide is recovered unchanged after boiling with concd. HCl or EtOH-KOH. Anhydrocotarnine-nitromethane is readily reduced to the methylamine, whose di-HCl salt, m.  $227^\circ$  and *picrate* m.  $200^\circ$  (decompn.) II. R. D. HAWORTH, W. H. PERKIN, JR., AND JOHN RANKIN *Ibid* 1444-8—Expts similar to the above were carried out with vanillin as the starting point. 3,4-Dimethoxybenzyl bromide, oil, decomps on distg in *vacuo* and has very slight lachrymatory powers. 6,7,3',4'-Tetramethoxy-2-benzylisoquinolinium bromide (VIII), m.  $137-8^\circ$ ; iodide, pale yellow, m.  $203-4^\circ$ . Cold NaOH gives 1-hydroxy-6,7,3',4'-tetramethoxy-2-benzyl-1,2-dihydroisoquinoline (IX), amorphous and forming a plastic mass on exposure to the air. VIII, heated with a large excess of EtOH-KOH, gives 6,7,3',4'-tetramethoxy-2-benzyl-1-isoquinoline, m.  $124-9^\circ$ . VIII and KCN give the 1-cyano deriv corresponding to IX, m.  $117^\circ$  (decompn.), rapidly loses HCN in dil acids. Reduction of VIII with Sn and HCl gives the 6,7,3',4'-tetramethoxy-2-benzyl-1,2,3,4-tetrahydroisoquinoline (X), m.  $93^\circ$ , this does not react with  $HCH(OMe)_2$ ,  $MeCH(OEt)_2$  or  $HO_2SCH_2CO_2H$ . Oxidation of X by 1 gives 6,7,3',4'-tetramethoxy-2-benzyl-3,4-dihydroisoquinolinium iodide, orange, m.  $184-5^\circ$ ; *periodide*, brown, m.  $160^\circ$ , *chloride* (XI), yellow, m.  $52-6^\circ$  (contains  $H_2O$  of crystn). XI and NaOH give the amorphous  $\psi$ -base, while EtOH-KOH or alk.  $K_2Fe(CN)_6$  gives the corresponding isoquinoline, amber, m.  $116^\circ$ . XI and KCN give the  $\psi$ -cyanide, m.  $98^\circ$ , whose EtOH solns exhibit a green fluorescence. 6,7,3',4'-Tetramethoxy-2-benzyl-1-nitromethyl-1,2,3,4-tetrahydroisoquinoline, m.  $148-9^\circ$ ; reduction splits off  $MeNH_2$ . III. R. D. HAWORTH AND W. H. PERKIN, JR. *Ibid* 1448-53—6-Nitro-*veratrylnorhydrodrastinine*, pale yellow, m.  $149-50^\circ$ , slowly becomes green in the air. Reduction with Zn dust gives an amine, which gives a greenish blue color with  $FeCl_3$ . HCHO gives an addn. product but on treatment with HCl this yields no trace of nitrotetrahydroberberine. Nitration of tetrahydroberberine gives the 6-nitro deriv, buff-colored, m.  $135^\circ$ . Since the above failure may be due to the inhibiting effect of the  $NO_2$  group, 6'-bromohomoveratrylhomoapaperonylamine, m.  $159-60^\circ$ , was prepd from bromobemoveratric acid and homopiperonylamine; heating with  $POCl_3$  in PhMe gave 6'-bromoveratryldihydroisoquinoline, which was reduced by Zn and  $H_2SO_4$  to 6'-bromoveratrylnorhydrodrastinine (XII), m.  $159-60^\circ$ , HCl salt, softens  $250^\circ$ , m.  $260-2^\circ$ ; *picrate*, orange, m.  $174-5^\circ$ . HCHO gives the 2-hydroxymethyl deriv, oil, whose *picrate*, yellow, m.  $154-5^\circ$ ; heating with HCl gives the unchanged compd, or splits off the  $HOCH_2$ -group. XII formate, heated at  $180^\circ$  for 3 hrs, gives the 2-formyl deriv, which was heated with  $POCl_3$  and then reduced, yielding tetrahydro $\psi$ -berberine, m.  $177^\circ$ . This shows that, rather than close the isoquinoline ring with the aid of the .CH group in the 2'-position of the veratryl nucleus, the tendency to ring closure in the 6'-position is so great that it will proceed in this direction even when the closure necessitates the elimination of the Br atom occupying that position.  $POCl_3$  and 2-formylveratrylnorhydrodrastinine give a good yield of dihydroanhydro $\psi$ -berberine, m.  $154-5^\circ$ . N-6-Nitrobenzoylnorhydrodrastinine m.  $160-1^\circ$ , not  $154^\circ$  (C. A. 18, 3385). Tetrahydroberberine on nitration yields a 6- $NO_2$  deriv., while the  $\psi$ -deriv. undergoes oxidation and does not yield a  $NO_2$  deriv.; this reaction may be used to distinguish the 2 types. IV. *Ibid* 1453-62.—This study deals with an attempt to convert papaveraline (XIII) into corydaline. XIII and 1 mol  $MeMgI$  give an orange addn product which regenerates XIII on decompn. with acid; 2 mols  $MeMgI$  give 7-demethylomethylpapaverinol (XIV), m.  $114-6^\circ$ ; solns. in dil acids are yellow but concd. acids give XV as does warming with phenylcarbimide. XIV could not be acetylated or methylated, XV being formed. XIV, warmed with 50%  $H_2SO_4$ , gives the anhydro deriv. (XV), m.  $151^\circ$ ; HCl salt, pale yellow; *perchlorate*, pale yellow, m.  $150^\circ$ . The base could not be acetylated or methylated and is stable when heated with KOH at  $180^\circ$ . Reduction of XV with Sn and HCl gives 7-demethylomethylpapaverine (XVI), m.  $148^\circ$ ; the *picrate*, *chromate*, *chloroplatinate* and *chloroaurate* are yellow ppts which become oily under boiling  $H_2O$ ; a nitrosamine could not be obtained. XVI also could not be methylated or acetylated. The reduction of XIV or XV with Sn and HCl yields 25% of 7-demethylomethylated tetrahydropapaverine, m.  $64-5^\circ$ ; *picrate*, orange, darkens  $210^\circ$ , m.  $225^\circ$  (decompn.); nitrosamine, m.  $124^\circ$ , gives the Liebermann reaction. XVI, heated in 50% HCl with gradual addn. of  $HCH(OMe)_2$ , gives 7-demethyl- $\psi$ -corydaline (XVII), m.  $150-1^\circ$ , and 2 amorphous bases, all of which yield the same *methiodide*, m.  $250^\circ$ ; the *methochloride* (XVIII), m.  $253^\circ$  (decompn.). XVII in EtOH-AcOH, treated with I and then with  $SO_3$ , gives dihydro-7-demethyl- $\psi$ -dehydrocorydalinium iodide, yellow, m.  $250^\circ$ , which is also obtained from nor- $\psi$ -corydalin by oxidation with  $Hg(OAc)_2$ . *Chloride*, yellow, m.  $235^\circ$  (decompn.); the concd.  $H_2SO_4$  soln is yellow, changed to a brilliant emerald-green on addn. of  $NaNO_2$  and then to a bright red. With excess of KOH it yields

keto-7 demethylo- $\psi$  corydaline, m. 210°, which cannot be methylated or acetylated. XVIII, boiled with excess KOH, gives anhydro-7-demethylomethyl- $\psi$ -corydaline (XIX), obtained only as a resin; HCl salt, m. 228° (decompn.); HI salt, m. 232°; picrate, yellow, with 2 EtOH of crystn., froth to a turbid liquid at 130°, m. completely 165°.



(XVII)



(XIX)

C. J. WEST

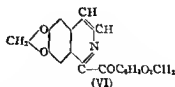
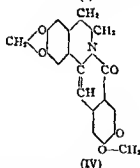
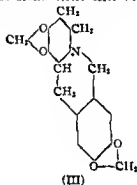
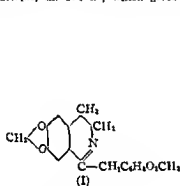
Constitution and synthesis of natural coloring matters. REX FURNESS. *Chem. Age* (London) 13, 30-3(1925).—A review on chlorophyll, the flavones, flavonols and anthocyanins.

Amino oxides of alkaloids of the tropane group. MAX POLONOVSKI AND MICHEL POLONOVSKI. *Compt. rend.* 180, 1755-7(1925).—Work analogous to that of Wolfenstein, Bamberger, Pictet, Freund, Valeur, Speyer and others on the action of  $H_2O_2$  on tertiary amines was extended to alkaloids in which the tertiary basic N was oriented in a bicyclic nucleus, viz., in a pyrrolidine and a piperidine ring. The alkaloid was treated either alone or in alc. or  $Me_2CO$  with a slight excess of  $H_2O_2$ , let stand several days, evapd. at a low temp., the residue extd. with  $Et_2O$ , in which the amine oxides were insol., and the residue crystd. whenever possible. All amine oxides were neutral to litmus, were extremely sol. in  $EtOH$  and  $H_2O$  and gave well-crystd. salts. They were reduced in cold  $H_2O$  by  $SO_2$  to sulfates of the original bases with simultaneous formation of *N* sulfonated ethers of the type obtained by Wolfenstein from trialkyl amine oxides or from *N* alkylpiperidine oxides. The sulfonated ethers hydrolyzed with great ease, partially in moist air and completely in boiling  $H_2O$ . Sulfonated ethers were not described by Mattison and Pictet in work on the reduction of strychnine oxide (*Ber.* 38, 2782(1903)), who reported its complete reduction. P. and P., however, obtained a sulfonated ether of strychnine oxide, m. 330°, slightly sol. in  $Na_2CO_3$  soln., and easily hydrolyzed when hot. Hyoscyamine *N*-oxide,  $C_{17}H_{23}NO_4$ , soft paste,  $ap -15^\circ$  (in  $EtOH$ )  $ap -19^\circ$  (in  $H_2O$ ); HCl salt m. 195°,  $ap -11.5^\circ$  (in  $H_2O$ ); *N*-sulfonated ether,  $C_{17}H_{21}O_5NSO_2$ , m. 208°,  $ap -15^\circ$  (in  $EtOH$  at  $75^\circ$ ), hydrolyzes when hot to hyoscyamine sulfate but when cold to free hyoscyamine. By proper control of the temp., complete racemization into atropine can be brought about. Atropine *N*-oxide, hygroscopic sirup, also obtained by racemization of the hyoscyamine *N*-oxide; HCl salt m. 192-3°; *N*-sulfonated ether m. 205°. Tropine *N*-oxide, prepd. either from  $H_2O_2$  and tropine or by sapon. of atropine *N*-oxide, m. 238° (decompn.); HCl salt m. above 250°; *N*-sulfonated ether m. 218°. Apodropine *N*-oxide, from  $Me_2CO$ , m. 128°; HCl salt m. 205°; salicylate m. 152°; *N*-sulfonated ether m. 155°. Homatropine *N*-oxide m. 138-40°; HBr salt m. 238°; *N*-sulfonated ether m. 210°. Scopolamine *N*-oxide, sirup,  $\alpha_D -14^\circ$  (in  $H_2O$ ); HBr salt m. 153°; perchlorate m. 167°; *N*-sulfonated ether.

C. C. DAVIS

Synthesis of 2,3,10,11-bismethylenedioxyprotuberine and 6,7,3',4'-bismethylenedioxyprotopapaverine. J. S. BUCK, WM. H. PERKIN, JR., AND T. S. STEVENS. *J. Chem. Soc.* 127, 1462-72(1925).—This work was undertaken to prep. substances bearing the same relation to protopine as epiberberine and its derivs. bear to cryptopine; the compds. are probably related to the  $\psi$ -base.  $ClH_2O, C_{24}H_{27}CH_2CH_2NHCOCH_2C_6H_5$ ,  $O_2CH, H_2O$ , and  $POCl_3$  in  $PhMe$  give 6,7,3',4'-bismethylenedioxy-3,4-dihydroprotopapaverine (I), m. 92-6° (picrate, pale yellow, m. 220° (decompn.)); it oxidizes quickly in the air. The crude I is easily reduced by Zn and  $H_2SO_4$  to the 1,2,3,4-tetrahydro deriv. (II), m. 84-5°, in 70-5% yields. III salt, m. 250-4°; picrate, bright orange, softens 190°, m. 210° (decompn.). II, treated with  $HCHO$  in  $MeOH$  contg.  $Na_2CO_3$  and the gum which ppt. dissolved in hot concd. HCl, gives 2,3,10,11-bismethylenedioxytetrahydroprotuberine (III), m. 214°. Oxidation of III with I in  $EtOH-AcOH$  gives 2,2,10,11-bismethyl-

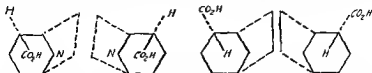
*enedioryprotoberberinium iodide*, bright yellow, which has a bitter taste and does not m.  $300^{\circ}$ ; the *chloride*, bright yellow, crystals with  $2\text{H}_2\text{O}$ , loses  $1\text{H}_2\text{O}$  at  $110^{\circ}$ ; from  $\text{Ac}_2\text{O}$  it seps. as anhyd., pale yellow needles, does not m.  $300^{\circ}$ . *Picrate*, bright orange-yellow, darkens above  $260^{\circ}$ , explodes  $310^{\circ}$ . The *chloride*, heated with  $\text{KOH}$  at  $100^{\circ}$ , gives a mixt. of 2,3,10,11-bismethylenedioxyxyprotoberberine (IV), pale yellow, m. above  $270^{\circ}$ , insol. in hot dil.  $\text{HCl}$ , and bismethylenedioxydihydroprotoberberine, bright yellow, m.  $161-4^{\circ}$  (*picrate*, Au-brown, decomps. above  $240^{\circ}$ ). I in  $\text{Et}_2\text{O}$ - $\text{MeOH}$ , exposed to the air for 10 days, gives 6,7,3',4'-bismethylenedioxy-9-keto-3,4-dihydroprotopapaverine (V), m.  $136^{\circ}$ ; it gives sol. yellow mineral salts; *HI* salt, yellow, m.  $216-9^{\circ}$  (decompn.); *picrate*, orange-yellow, m.  $202^{\circ}$  (decompn.); *oxime* m.  $235^{\circ}$  (decompn.). V, heated with  $\text{MeOH}$ - $\text{KOH}$  for 30 min, gives 50% of 6,7,3',4'-bismethylenedioxy-9-ketoprotopapaverine (VI), m.  $186^{\circ}$ ; the concd.  $\text{H}_2\text{SO}_4$  soln. is deep orange-red. *HI* salt, yellow, darkens  $210^{\circ}$ , m.  $230^{\circ}$  (decompn.), completely hydrolyzed by hot  $\text{H}_2\text{O}$ ; *picrate*, yellow, m.  $240^{\circ}$  (decompn.); *oxime* m.  $275^{\circ}$  (decompn.). Reduction with  $\text{Zn}$  in  $\text{AcOH}$  gives 6,7,3',4'-bismethylenedioxy-9-hydroxyprotopapaverine, m.  $160-70^{\circ}$ ; the concd.  $\text{H}_2\text{SO}_4$  soln. is deep bluish violet, turning yellowish brown on addn. of  $\text{KNO}_3$ . The  $\text{AcOH}$  soln., satd. with  $\text{HBr}$  and reduced with  $\text{Zn}$  powder, gives 6,7,3',4'-bismethylenedioxyprotopapaverine, m.  $170-2^{\circ}$ , which gives an intense bluish violet color with concd.



$\text{H}_2\text{SO}_4$ ; *picrate*, pale yellow, m.  $199-202^{\circ}$ . Oxidation of tetrahydropapaverine with I in  $\text{EtOH}$  gives 6,7,3',4'-tetramethoxy-9-keto-3,4-dihydroprotopapaverine, m.  $190-1^{\circ}$ .  
C. J. WEST

Isomeric compounds of hydroecgonidine. S. KIMATSU AND S. INOUE, *J. Pharm. Soc. Japan* No. 518, 354-67 (1925).—According to Gadamer (*C. A.* 17, 1025), hydroecgonidine prepd. by reducing anhydroecgonine by Willstätter's method of  $\text{NaOAc}$  (I) and by Paal-Skita's catalytic method with  $\text{Pd}$  (II), produces 2 different Au salts, which when converted into the  $\text{HCl}$  salt produce 2 different *l*-rotatory compds., both of which m.  $233^{\circ}$ , while hydroecgonidine produced by G.'s method of treating with  $\text{Zn} + \text{H}_2\text{SO}_4$  (III), gives one Au salt, and its  $\text{HCl}$  salt, m.  $233^{\circ}$ , but is *d*-rotatory. According to K. and I., hydroecgonidine cannot be prepd. in a pure state unless there is used a pure anhydroecgonine, which cannot be obtained by simple purification with solvents or distn. as an ester. Following on Einhorn's method, K. and I. first converted anhydroecgonine into the  $\text{HI}$  salt (m.  $202.5-3.5^{\circ}$ ), which is converted to the  $\text{HCl}$  salt (m.  $241^{\circ}$ ), and distd. as the ester

(b<sub>1</sub>, 137–10°) With this pure compd, G's work was repeated. I.HCl, m. 233–15°, but the HCl salts of II and III, m. 263°, 262°, resp.,  $[\alpha]_D^{25}$  of the HCl salt of I is –4.64°, of that of II 1.22°, and of that of III, 2.23°. Two Au salts obtained from I, m. 211° and 231°, those obtained from II, 198°, 208°, and those from III, 199°, 209°. If II is heated with NaOAc at 130°, for 5 hrs, it now m. 233–4°,  $[\alpha]_D^{25}$  –2.15°, and the 2 Au salts m. 210°, 231°, resp., and are identical with those of I. Thus there are 4 Au salts of hydroecgonidine. Accordingly, there are 4 isomers of hydroecgonidine, viz normal *d* hydroecgonidine A (Au salt, m. 198–9°), B (Au salt, m. 208–9°),  $\psi$ -4 hydroecgonidine A (Au salt, m. 211°), and B (Au salt, m. 231°), and then spacial relations are probably as follows



Synthesis of androsin. F. MAUTHNER, *J. prakt. Chem.* 110, 123–4 (1925).—Androsin, isolated by Moore from the rhizome of *Apocynum androsaemifolium* (C. A. 2, 2962), m. 223–4°, is identical with the synthetical *d* glucoacetovanillone of M. (C. A. 13, 1310).

Saponins. III. The saponin occurring in *Sapindus saponaria* L. and *Sapindus mukorossi* utilis (Trabuti). W. A. JACOBS, *J. Biol. Chem.* 64, 379–81 (1925).—The saponin obtained from both *Sapindus saponaria* L. and *Sapindus mukorossi* utilis (Trabuti) was identified as *hederagenin*, by isolation of the Me ester and its acetonide deriv. Cf. C. A. 19, 2056.

Strophanthin. VII. The double bond of strophanthidin. W. A. JACOBS AND A. M. COLLINS, *J. Biol. Chem.* 64, 383–9 (1925), cf. C. A. 18, 2170, 19, 1142, 1281.—Sapon of dianhydrostrophanthidin yields *dianhydrostrophanthidinic acid*, C<sub>11</sub>H<sub>15</sub>O<sub>6</sub>, m. 215–8°,  $[\alpha]_D^{25}$  –170°, (c 0.51 in equal vols of CHCl<sub>3</sub> and EtOH) which showed no indication of the formation of a lactone. The same acid was obtained by boiling the ethylal of oxidodianhydrostrophanthidinic acid with 2% HCl in 50% EtOH. On the other hand, the ethylal of oxidodihydrodianhydrostrophanthidinic acid, upon sapon with NaOH and acidification with HOAc yielded a mixt. of the free *oxidodihydrodianhydrostrophanthidinic acid*, m. 197–202°, and the lactone, to which the free acid changes very readily. The ethylal formed no oxime, only the lactone. But the ethylal of *oxidodianhydrostrophanthidinic acid* readily formed an oxime, C<sub>11</sub>H<sub>15</sub>O<sub>6</sub>N, m. 170–2°. These observations are believed to indicate that strophanthidin and its anhydro derivs are lactones of an enolized, presumably  $\gamma$ -ketonic acid, which when once opened are prevented from closing again by the stability of the ketonic form. This condition disappears on hydrogenation or when the double bond is shifted under the influence of alkali with the formation of the internal ester of a sec alc.

Polysaccharides. XXIX. Chitin. II. The configuration of glucosamine. P. KARRER, O. SCHNIDER AND A. P. SMIRNOV, *Helv. Chim. Acta* 7, 1039–45 (1924).—When fructosamine is distd with zinc dust a mixt, chiefly composed of 2,5 dialkylpyrazines, is obtained. This, and other observations, lead to the conclusion that the mol. unit of chitin (cf. C. A. 17, 988) is not composed simply of 2 glucosamine residues.

R. C. A.

Simultaneous action of Al<sub>2</sub>O<sub>3</sub> and Fe at high temperatures and pressures (PATENT, KLUKVIN) 2. Color and molecular geometry (Moir) 2. The electrolytic oxidation of alcohols. 1. Chlorination of ethyl alcohol (Kornzumi) 4.

ADKINS, HOMER and McILVAIR. *Practice of Organic Chemistry in the Laboratory*. New York: McGraw-Hill Book Co. 248 pp. \$2.25.

HAUSER, FRITZ. *Untersuchung des Chrysarobins und seiner Bestandteile*. Weida (Thür.). Thomas & Hubert. 132 pp.

KEHRMANN, FRÉDÉRIC. *Gesammelte Abhandlungen*. Vol. 3. Part 1: Untersuchungen über Oxoniumverbindungen. Part 2: Untersuchungen über Thionium- und Sulfoniumverbindungen. Part 3: Untersuchungen über Alkridin und Karbazinfarbstoffe. Leipzig: G. Thieme. 495 pp.

$\alpha$ -Naphthylamine. G. POMA and G. PELLEGRINI. Brit. 227,481, Aug. 27, 1923.  $\alpha$ -Nitronaphthalene is catalytically reduced to  $\alpha$ -naphthylamine by heating and agitation in an autoclave with  $H_2O$ ,  $H$  and a catalyst such as finely divided  $Ni$ ,  $Co$ ,  $Cu$  or  $Fe$  or one of their oxides and a carrier such as pumice, charcoal or quartz. The starting material should be free from org. halogen compds.,  $S$ ,  $Te$  and  $Se$ .

Benzyl citrates. F. HEFTI and W. SCHULT. Brit. 227,232, Oct. 31, 1923. Benzyl citrates are made by benzylating citric acid or  $Na$  or  $K$  citrate with benzyl alc. or a benzyl halide. The tri- and di-benzyl esters may be used as therapeutic agents. The  $Na$ ,  $Ca$ ,  $Fe$  and  $Ag$  salts of dibenzyl citrate are prepd. by reaction of the ester with  $NaOH$ ,  $CaCl_2$ ,  $FeCl_3$  and  $AgNO_3$ , resp.

Methanol, etc. BADISCHE ANILIN & SODA FABRIK. Brit. 227,147, Aug. 28, 1923.  $MeOH$  and other  $O$ -contg. org. compds. are prepd. by the catalytic reduction of  $C$  oxides (preferably  $CO$ ) with a mixt. of oxides of metals of different groups as catalyst, e. g.,  $ZnO$  with an oxide of  $Cr$ ,  $U$ ,  $V$  or  $W$ ;  $Mg$  and  $Mo$  oxides,  $Ce$  and  $Mn$  oxides, or  $Cd$  and  $Cr$  oxides. A  $Cu$  app. is used and the catalysts should be free from  $Fe$ ,  $Ni$  and  $Co$ .

Methanol and methylene chloride. T. GOLDSCHMIDT AKT.-GES. Brit. 227,475, Jan. 10, 1924.  $MeOH$  and  $CH_2Cl_2$  are sep'd from the chlorination products of  $CH_4$  by forcing the latter (first freed from  $HCl$ ) into milk of lime to saponify the  $MeCl$  content to  $MeOH$ , which remains in the sapon. vessel.  $CH_2Cl_2$  is then sep'd from the residual gases by cooling under pressure. Remaining gases are returned to the chlorination process.

Calcium oxalate, etc., from plant materials. W. A. FRAYMOUTH and BHOPAL PRODUCE TRUST, LTD. Brit. 227,925, Oct. 25, 1923.  $Ca$  and other oxalates occurring naturally in plants such as those of the genus *Opuntia* are recovered by disintegrating the plant and treating the pulp obtained by froth-floatation. Tannin, sesame oil and eucalyptus oil may be used.

Organic acids from vegetable materials. W. A. FRAYMOUTH and BHOPAL PRODUCE TRUST, LTD. Brit. 227,924, Oct. 25, 1923. *Tamarindus indica* fruit is pulped, fibrous matter and seeds are removed and the pulp is treated with milk of lime and may then be passed through a sieve on to a traveling belt of crepe rubber to which the  $Ca$  tartrate tends to adhere.  $Cu$  tartrate, oxalates and other salts of org. acids may be similarly recovered from vegetable materials.

Purifying ether. J. P. FOSTER. U. S. 1,544,569, July 7. Ether bearing vapors are passed upwardly through a scrubbing tower counter-current to a neutralizing soln. such as  $NaOH$ , which is maintained at a temp. that will vaporize the ether and condense other accompanying vaporous substances.

## 11—BIOLOGICAL CHEMISTRY

PAUL E. HOWE

### A—GENERAL

FRANK F. UNDERHILL

Physico-chemical studies on proteins. II. Alkali binding—comparison of the electrometric titration of proteins and of phosphoric acid with sodium and calcium hydroxides. W. F. HOFFMAN and R. A. GORTNER. *J. Phys. Chem.* 29, 760-81 (1925).— $H_2PO_4$  and the proteins, casein and durumin, have been titrated electrometrically with both  $NaOH$  and  $Ca(OH)_2$ , and 'back-titrated' with  $HCl$ . The alkali titration curves of casein and fibrin show binding of alkali at about  $pH$  5.5 and resemble the curve for a weak acid such as  $NaH_2PO_4$ . Other proteins, of which durumin is a type, behave as much weaker acids, beginning to bind alkali only at about  $pH$  10.0. Curves of the same type are obtained when a protein is titrated with either  $NaOH$  or  $Ca(OH)_2$ . When  $H_2PO_4$  is titrated with  $NaOH$  and  $Ca(OH)_2$ , the 2 curves are not similar. In the latter case both the secondary and tertiary hydrogens are replaced by  $Ca$  at the same  $pH$ , at which  $NaH_2PO_4$  is formed. The titration curves of protein with alkali and  $H_2PO_4$  with alkali are not identical at similar  $pH$  values with the curves formed by a subsequent 'back titration' with  $HCl$ . There is a 'lag' in the back titration curves. This 'lag' is shown to be due to the fact that the reaction  $CaH_2(PO_4)_2 + 4HCl = 2CaCl_2 + 2H_2PO_4$  does not go to completion, resulting in an equil. and the presence of free  $HCl$ , which increases the  $pH$ . All 3 hydrogens of  $H_2PO_4$  may be titrated by  $Ca(OH)_2$  below  $pH$  8.0. The bearing of this observation on the structure of the  $Ca$  phosphates is discussed.  $Ca_3(PO_4)_2$  is apparently stable in solns. as acid as  $pH$  6.5." F. L. B.

Changes in the sweetening power of dulcin (*p*-phenetylcarbamide) by chemical modification. H. THOMAS. *Deut. Zuckerind.* 49, 1056(1924).—Replacement of one of the amino-H atoms in *p*-phenetylcarbamide by an alkyl group decreases the sweetness. Introduction of a second carbamido group in the  $\alpha$ -position to the first causes a similar loss of sweetening power. Conclusion: For the production of flavor the presence of 1 or more "sapphoric" groups alone is not sufficient, but these groups must occupy definitely related positions (cf. Bergmann, Camacho and Dreyer, C. A. 17, 996).

Chemical and clinical investigations on plastein problems. E. HASSE. *Arch. Verdauungskrankh.* 31, 275-84(1923). *Chem. Zentr.* 1924, I, 2370-80.—Plastein protein was obtained from Witte's peptone by the action of papain or rennet in a soln. of pH 2.8 to 5.4. In its formation there was a decrease in the free amino groups. In acidities greater than 2.8 there was no formation of this protein. It is not formed in the presence of inactivated enzymes. Plastein contains less N and more S than animal proteins.

Some thoughts on the central position of carbohydrates in the organic world. E. ABDERHALDEN. *Biochem. Z.* 156, 51-3(1925).—Review and discussion of the present knowledge of carbohydrate metabolism.

The relation of blood sugar to glycogen. H. PRINGSHEIM. *Biochem. Z.* 156, 109-17(1925).—A theoretical development of the concept of glycogen synthesis from glucose through the labile  $\lambda$  form.

The increase of colloidal swelling through chemical means. M. POROFF AND K. SMISORF. *Biochem. Z.* 156, 97-108(1925).— $\text{CH}_2\text{O}$ , glycerol, phthalic acid, Mg and Mn salts, etc., caused an increase in the swelling of gelatin in aq. soln. An optimum concn. for each was found at which max. effect was noted. The application of the results to biological problems is discussed.

Nephelometric investigation of glycogen decomposition by salivary diastase. J. PARCHTNER. *Biochem. Z.* 156, 249-54(1925).—The nephelometric method for the detn. of glycogen developed by M. Cremer is applicable to a detn. of the glycogen hydrolysis rate by salivary diastase. The method and typical results of measurements of the rate of hydrolysis of glycogen by salivary diastase are presented.

Insulin and sugar partition between liquid and non-liquid systems. H. HAUPLER AND O. LOEWI. *Biochem. Z.* 156, 203-9(1925).—When ground-up pig arteries or washed blood corpuscles are shaken with a NaCl-glucose soln. contg. insulin and then filtered a decrease in the concn. of glucose in the filtrate was observed. When insulin was omitted no decrease was observed. The relation of these results to the theory that in diabetes there is a disturbance in the permeability of the cells for glucose is discussed.

Sulfatase. V. Animal sulfatase. C. NEUBERG AND E. SIMON. *Biochem. Z.* 156, 363-73(1925); cf. C. A. 18, 3610.—It was demonstrated that the liver, kidneys, brain and muscles of rabbits contain an enzyme capable of hydrolyzing sulfuric acid esters, as follows:  $\text{ROSO}_3\text{K} + \text{H}_2\text{O} \rightarrow \text{ROH} + \text{KHSO}_4$ . A 4 to 18% hydrolysis of phenylsulfuric acid was obtained from freshly prepd. tissue in 6 to 11 days. Aq. exts. of this new animal enzyme, and also dry preps., may be prepd.

Carboligase. VIII. Biochemical acyloin synthesis. C. NEUBERG AND E. SIMON. *Biochem. Z.* 156, 374-8(1925); cf. C. A. 18, 2181; 19, 305.—Acetoin is formed when  $\text{CH}_3\text{CHO}$  is added to a yeast suspension contg. glucose or sucrose. Acetoin is not formed in a yeast washed free of carbohydrate. This carboligase synthesis is regarded as the simplest case of coupled bio-synthesis of carbohydrates.

Alexander Ellinger (1870-1923). PHILIP ELLINGER. *Ergebnisse Physiol.* I Abt. 23, 139-79(1924).—An obituary containing an account of E.'s work and a complete bibliography of his publications.

Professor Robert Tigerstedt. C. G. SANTÉSSON. *Ergebnisse Physiol.* II Abt. 23, 268-72(1925).—An obituary with a portrait.

H. J. Hamburger. J. DE HAAN. *Ergebnisse Physiol.* II Abt. 23, 273-6(1925).—An obituary.

Carl von Hess. LEON ASHER. *Ergebnisse Physiol.* II Abt. 23, 277-83(1925).—An obituary.

Porphyryns from blood pigment. A. PARENDECK AND K. BONATH. *Z. physiol. Chem.* 144, 60-7(1925).—The formation of porphyrin from hematin may be demonstrated by 2 procedures: (a) by heating a soln. of hematin in glacial AcOH with  $(\text{NH}_4)_2\text{H}_2\text{O}$ , which gives a porphyrin believed to be identical with  $\alpha$ -hematoporphyrin, and (b) electrolytic reduction of hematin with a porcelain diaphragm and Cu cathode, whereby 3 porphyrins are obtained, which are probably  $\alpha$ -hematoporphyrin, Nencki's

porphyrin and mesoporphyrin. Electrolytic reduction and also catalytic hydrogenation of  $\alpha$ -hematoporphyrin in  $\text{H}_2\text{SO}_4$ -MeOH soln. in the presence of colloidal Pd give mesoporphyrin.  $\alpha$ -Hematoporphyrin is probably identical with hemateric acid,  $\text{C}_{20}\text{H}_{14}\text{O}_4\text{N}_4$ . The soly. of mesoporphyrin in  $\text{CHCl}_3$  also is pointed out. A. W. DOX

Protein and potassium ions. W. E. RINGER. *Z. physiol. Chem.* 144, 85-96 (1925).—Nucleoproteins dissolved in KOH to neutral soln. depress somewhat the K-ion activity. If a mol wt. of 50,000 is assumed for the protein, 1 mol. would unite with 1 or 2 K ions. Euglobulins dissolved in KCl do not bind K ions; on the other hand Cl ions are appreciably bound. Again with a mol wt. of 50,000, each mol. would bind 10 Cl at a concn. of 0.14 N KCl. In alk soln (KOH) euglobulins depress the K-ion activity, each mol. binding approx. 2 K. In such solus, however, each mol. of protein binds some 14 OH ions. In contrast to the binding of OH in alk. soln. and of Cl in neutral soln., the binding of K by euglobulins and nucleoproteins is extremely small. Hemoglobin and oxyhemoglobin at neutral and also acid reaction do not appreciably bind K or Cl. In 0.005 N KOH each mol binds 1 K, and with greater alkalinity the binding is somewhat greater. Water-sol. protein (hemoglobin) appears to bind no ions at neutral reaction. Insol proteins (nucleoproteins, euglobulins) at neutral reaction bind either a trace of cation or somewhat more anion. A. W. DOX

"Natural" hematin-like pigments and porphyrins related to them. Preliminary paper. O. SCHRAM. *Z. physiol. Chem.* 144, 272-5 (1925).—From the crude "hematin" obtained from feces a porphyrin was prepd. by removal of Fe. This porphyrin is similar to eoporphyrin in the spectroscopic behavior of its alk. soln. and its insoly. in  $\text{CHCl}_3$ , but differs from both eoporphyrin and mesoporphyrin in the spectra of its  $\text{Et}_2\text{O}$  and HCl soln. and of its Fe complex. Its  $\text{Et}_2\text{O}$  spectrum resembles that of etioporphyrin. A porphyrin probably identical with it was also obtained from a hematin-like pigment found in human blood after bacterial decompn. A. W. DOX

Constitution of the proteins. MAX BERGMANN. *Z. physiol. Chem.* 144, 278-7 (1925).—Polemical against Abderhalden (*C. A.* 19, 1715, 2033). A. W. DOX

The bile acids. XII. Investigation of a concretion from the rennet bag of a goat. MARTIN SCHENCK. *Z. physiol. Chem.* 145, 1-17 (1925); cf. *C. A.* 18, 3601.—A 160-g. stone removed from the rennet bag of a 2-year-old goat contained 75% cholic acid and 5% choleic acid. Higher fatty acids and cholesterol were present in small quantity. Unaltered bile pigment could not be demonstrated with certainty. The remainder of the stone consisted of amorphous substances, including vegetable matter and ash. XIII. The occurrence of desoxycholic (choleic) acid in the saponified bile of the goat. *Ibid* 95-100.—Cholic acid was obtained in a yield of about 4% and choleic acid 0.4% of the original bile. The proportions were, therefore, 1:10 as compared with 1:15 in the concretion from the rennet bag. A. W. DOX

Arginase. S. EDLBACHER AND P. BONEM. *Z. physiol. Chem.* 145, 69-90 (1925).—The optimum  $p_H$  for arginase is 9.5-9.8. Under favorable conditions the enzymic cleavage of arginine is nearly quant. Guanidineacetic acid, guanidinepropionic acid, agmatine, arginine-methyl ester and L-arginine are not hydrolyzed by arginase. Only  $\frac{1}{4}$  of the arginylarginine mol. is hydrolyzed, probably the half contg. the free carboxyl. Arginase was not found in the intestinal mucosa of the dog, cat or pigeon. The liver of cat, mouse, dog, calf, guinea pig, frog and man contained a considerable amt., but that of the pigeon showed only traces. While mere traces were present in the liver of the hen, that of the cock contained an abundance of the enzyme, indicating a fundamental difference in the arginine metabolism of the 2 sexes. Testes of cocks, pigeons, bull and guinea pig contained considerable arginase, but those of calves contained very little, showing thus a difference in function of the organ before and after puberty. On the other hand, ovaries of hens, pigeons and dogs showed very little arginase, an exception being those of a brooding pigeon. By means of the formol-titration arginase could not be demonstrated in the kidneys of birds, but by the urease method it was demonstrated in the kidneys of fowl and pigeons of both sexes. The kidneys of dog, cat, rabbit, mouse and guinea pig contain varying amts. of arginase, but none was present in the spleen of these animals. The suprarenals of the guinea pig were free from the enzyme. At the time of ovulation the livers of ducks and hens contain arginase, but not the ovaries. A. W. DOX

Sucrase. V. HANS V. EULER AND KARL JOSEPHSON. *Z. physiol. Chem.* 145, 130-43 (1925); cf. *C. A.* 18, 2531.—The hypothetical division of sucrase into an active and an inactive component is in agreement with Willstätter's and Schneider's (*C. A.* 19, 1713) conception of this enzyme as a mol. consisting of a chemically functioning active group and a colloidal carrier. The inactive component or "protein-like portion" previously reported meets all the requirements of a colloidal carrier. If inverting power

is taken as a measure of enzyme purity, 2 assumptions are valid, (1) the existence of a single species of sucrose with const activity and (2) the presence of the entire enzyme in an active form. *i. e.*, any inactivated portion may be disregarded. The latter assumption is not valid for the reason that re activation of the inactivated enzyme has been accomplished by warming. The sensitivity of the enzyme to trypsin may be explained by an actual destruction of a peptide-like component, or by a decrease in stability due to destruction of the protective colloid. The fact that purified sucrose preps. of high activity may or may not show a high tryptophan content indicates the existence of a tryptophan-free sucrose and possibly a plurality of sucrases. A. W. D.

Glucose and fructose in solutions containing alkali and phosphate. HANS V. EULER and RAGNAR NILSSON. *Z. physiol. Chem.* 145, 184-93(1925).—The decrease in rotation of glucose solns. on the addn. of alkali is due to the formation of glucosate ions rather than to a shift in the equil. between the  $\alpha$ - and  $\beta$  forms. Addn. of phosphate, however, increases the rotation of both glucose and fructose. Measurements of *f-p.* depression show that a reaction occurs between fructose and phosphate whereby the total mol. concn. decreases. The effect increases strongly with decreasing acidity from *pH* 4.5 on. It is more marked with fructose than with glucose. The form of glucose present in the blood shows a greater affinity for phosphate than either the  $\alpha$ - or  $\beta$  form. A. W. D.

The natural porphyrins. XVI. Kämmerer's porphyrin. H. FISCHER and FRITZ LINDNER. *Z. physiol. Chem.* 145, 202-20(1925); cf. *C. A.* 19, 1714—Kämmerer's porphyrin was prepd. by bacterial decompn. of blood and of blood corpuscles in a bouillon medium.  $H_2S$  converted this into coproporphyrin,  $AcOH \cdot HBr$  into hematoporphyrin,  $AcOH \cdot HI$  into mesoporphyrin. The green pigment from egg shells after removal of the porphyrins was reduced by means of  $H_2$  to its leuco compd., and this when treated with diazobenzenesulfonic acid gave a red azo dye. The reaction corresponds to that of bilirubin acid. Reduction of the pigment with  $Na$  amalgam gave a leuco compd. which showed the typical urobilin fluorescence with alc.  $Zn(OAc)_2$  and an intense violet color with  $Cu(OAc)_2$ . Oxidation with  $HNO_3$  gave a cryst. substance, *m.* 57°, which was not methylethylmaleic imide. A. W. D.

Attempts to prepare S. Fränkel's and S. Kafka's glucosamine-containing phosphatide from brain. H. THIENFELDER and E. KLEVE. *Z. physiol. Chem.* 145, 221-8(1925).—Since the phosphatide gave the Molisch reaction it could not have been a pure substance. Prep'd. according to F. and S. (*C. A.* 14, 2002), with certain modifications the product showed the same *m. p.*, but after hydrolysis by 3 hrs. boiling with  $HCl$  which would destroy any galactose present but leave the glucosamine intact, no glucosamine was found. A. W. D.

New researches on maltase. VICTOR ESTIENNE. *J. pharm. Belg.* 6, 797-802, 813-9(1924).—Expts. were made on the germination of various molds on a maltose culture medium prep'd. by hydrolyzing starch with amylase. To det. if a mold contains maltase prep. a diastatic powder with the aid of young cultures, and place about 1.5 g. per 100 of this powder in direct contact with a 2% soln. of maltose. It is necessary to specify the manner in which the soln. of maltose is made (in the hot or cold) and to wait at least 2 hrs. before using if the polarimetric method, which is the most rapid and exact for following the hydrolysis, is used. Hydrolysis is always complete for 1-10% solns. of maltose with the maltase of *Aspergillus niger* and *Mucor boudard.* It is incomplete with maize, beetroot and nasturtium. The rapidity of decompn. varies with the temp. and the origin and quantity of maltase used. The maltase in the powdered molds studied was still active after a number of years. A. G. DuMEX.

Measurement of changes due to hydration of colloids, to altered permeability, and to growth. D. T. MACDOUGAL. *Carnegie Inst. Washington Year Book* 22, 46-7(1924); *Botan. Abstracts* 14, 110.—Studies by means of artificial osmotic cells, with various kinds of colloidal mixts. employed as membranes, are considered. H. G.

Oxidation of glucose by means of air. H. A. SPOHR. *Carnegie Inst. Washington Year Book* 22, 55(1924); *Botan. Abstracts* 14, 125.—Chem. studies are reported on glucose oxidation by the  $O$  of the air in darkness. H. G.

A comparison of the molecular weights of the proteins. G. S. ADAIR. *Proc. Camb. Phil. Soc. (Biol.)* 1, 75-83(1924); *Physiol. Abstracts* 9, 569.—By applying a new method of calcn. derived from the osmotic pressure of hemoglobin solns., it was found that the mol. wts. of 10 different proteins were in the neighborhood of 60,700, a figure much larger than any previous ests. H. G.

Chlorocruorin. H. M. FOX. *Proc. Camb. Phil. Soc. (Biol.)* 1, 204-18(1924); *Physiol. Abstracts* 9, 581.—Chlorocruorin is the red-green pigment dissolved in the blood of certain polychete worms; it is a respiratory pigment, for it can be alternately re-

duced by tissues and oxidized in the air. Eight derivs. analogous to those of hemoglobin have been prepd., and their absorption bands more or less closely resemble those of the latter, except that they are shifted towards the red end of the spectrum. The spectrum of reduced chlorocruorin differs from that of mammalian, and from that of *Arenicola* hemoglobin. The total O capacity of the blood of *Spirographis* is about  $\frac{1}{2}$  that of human blood. H. G.

Blood catalase and temperature of the surroundings. G. VIALE. *Rend. accad. Lincei* 33, 314-5(1924). *Physiol. Abstracts* 9, 573.—The amt. of catalase present in the blood increases as the temp. of the surroundings diminishes. H. G.

Oxidases in the blood at moderate altitudes. J. J. IZQUIERDO. *Rev. mexicana biol.* 4, 188-9(1924). *Physiol. Abstracts* 9, 573.—There is no change in the oxidase content of the blood in men, cattle, rabbits and guinea pigs at a height of 7000 ft. H. G.

The oxygen and carbon dioxide limits in the respiratory air. A. GRÖGLI. *Arch. Hyg.* 95, 160-73(1925).—The purpose of the research was to est. the limits of  $\text{CO}_2$  and  $\text{O}_2$  concn. compatible with life in resting guinea pigs, rats and mice under different temp. conditions. The first series of expts. was carried out under natural conditions in that the air in the glass box about the animals was frequently changed. The second series with artificial absorption of  $\text{CO}_2$  questioned whether life will endure with a smaller quantity of  $\text{O}_2$ . In the third series more  $\text{CO}_2$  was admitted than normally. In the fourth series  $\text{O}_2$  and  $\text{CO}_2$  were simultaneously admitted. Guinea pigs, rats and mice remained alive for 45-70 hrs. at 15-31° in the first series of expts. During this time the  $\text{CO}_2$  rose 14.6-15.9% and the  $\text{O}_2$  sank 4-5.2%. When the animals were kept at 32-34° or 2-5° most of them died at an  $\text{O}_2$  concn. of 7-8% and a  $\text{CO}_2$  concn. of 11.8-12.7%. If the  $\text{CO}_2$  was absorbed from the box the animal remained alive longer on the reduced  $\text{O}_2$  content—at most from 58 to 83 hrs., while the  $\text{O}_2$  content reduced to 3.1-3.4%. At 30-31° the ability to resist was less and the animals died with an  $\text{O}_2$  concn. of 4.9-5.8%. If the temp. was increased further to 32-34° or lowered to 3-3° then the demand for  $\text{O}_2$  was greater, and death occurred at an  $\text{O}_2$  concn. of 6-7%. When the  $\text{CO}_2$  content was increased to 12.6-17.2% at room temp. the animals lived 20 hrs. The  $\text{CO}_2$  rose in this time to 20.8-22.7% while the  $\text{O}_2$  fell to 9.6-12.8%. With the simultaneous artificial increase in  $\text{O}_2$  and  $\text{CO}_2$  content the animal tolerated more  $\text{CO}_2$ . If the  $\text{O}_2$  concn. was increased to 33-39% at room temp. then the  $\text{CO}_2$  content rose 24-25.2% and even 28% at 30-31°. All expts. were carried out in parallel without and with partial absorption of the water vapor which was formed. The min. limit of tolerance to  $\text{O}_2$  and the max. tolerance to  $\text{CO}_2$  is not const.; it is dependent upon temp. By decreasing the  $\text{CO}_2$  concn. the min.  $\text{O}_2$  necessary is lowered. With increased  $\text{O}_2$  content the limit of  $\text{CO}_2$  tolerance is raised. F. B. SEIBERT

Proteins of wheat bran. II. Distribution of nitrogen, percentages of amino acids and of free amino nitrogen: a comparison of the bran proteins with the corresponding proteins of wheat endosperm and embryo. D. B. JONES AND C. E. F. GERSDORFF. *J. Biol. Chem.* 64, 241-51(1925); cf. *C. A.* 18, 693.—By the Van Slyke method (*C. A.* 5, 1938) for free amino-N and for the detn. of the bases, those of Folin and Looney (*C. A.* 16, 1790) for cystine and tyrosine and that of May and Rose (*C. A.* 17, 116) for tryptophan, the following values were obtained: bran prolamine, free  $\text{NH}_2\text{-N}$  1.88%, cystine 2.29%, arginine 4.41%, histidine 0.84%, lysine 2.45%, tryptophan 1.37%, tyrosine 3.38%, bran albumin, free  $\text{NH}_2\text{-N}$  2.84%, cystine 3.29%, arginine 10.04%, histidine 2.57%, lysine 4.51%, tryptophan 4.76% and tyrosine 4.20%; bran globulin, free  $\text{NH}_2\text{-N}$  6.59%, cystine 1.52%, arginine 14.13%, histidine 2.76%, lysine 11.84%, tryptophan 2.85% and tyrosine 3.69%. The high content of the so-called essential amino acids is emphasized. I. GREENWALD

Nature of heat denaturation of proteins. HSIEN WU AND DAISY YEN WC. *J. Biol. Chem.* 64, 369-78(1925); cf. *C. A.* 19, 1870.—In the heat denaturation of proteins, there is an increase in the capacity to bind acids and bases and an increase in the reactivity with the Folin-Denis phenol reagent. The filtrate obtained from the tungstic acid pptn. of a heated albumin soln. gives a more intense reaction with the phenol reagent than does a similar filtrate from unheated protein. Heat denaturation is, therefore, like acid and alkali denaturation, accompanied by hydrolysis. I. G.

The globulins of the jack bean (*Canavalia ensiformis*). II. The content of cystine, tyrosine and tryptophan. J. B. SUMNER AND VIOLA A. GRAHAM. *J. Biol. Chem.* 64, 257-61(1925); cf. *C. A.* 13, 847.—The proteins of the jack bean were purified in the following manner. *Concanavalin B*. (B) Mix 1 kg. of meal with 2 l. 30-35% EtOH for 0.5 hr. Press out, centrifuge and allow liquid to stand overnight at -10°. Decant the supernatant liquid and centrifuge the remainder. Stir the ppt. with dil. neutral phosphate soln. Crystals of I sep. out. Centrifuge and wash twice with 2% EtOH.

cation in an atm. dried by  $H_2SO_4$ . The vitality of the tissues was measured by the respiratory exchanges at the moment under consideration. This respiration is in general more active in the energetic tissues (brain, heart and muscles) which carry the most water and the highest concn. of oxidases. It is only the combined water of the protoplasm which maintains the work of osmosis and the nutritive phenomena the essence of which remains diastatic. The biochem. causes of this proportion of combined water and its influence upon the surface tension of the medium are undetd. L. W. RIGGS

Active protoplasmic mass and protein of reserve. T. KAHN. *Compt. rend.* 180, 1685-7 (1925).—A general discussion in which the views of Benedict, Terroine and others are considered. L. W. RIGGS

Biologic bearing of certain geochemical manifestations of life. V. VERNADSKII. *Rev. gen. sci.* 36, 301-4 (1925).—A theoretical application to biological chemistry is made of recent discoveries in the field relating to the structure of the C atom. L. W. RIGGS

Induced oxidation of carbohydrates. C. C. PALIT AND N. R. DHAR. *J. Phys. Chem.* 29, 799-807 (1925).—Starch, maltose, arabinose, levulose, galactose, lactose and cane sugar are oxidized to  $CO_2$  and  $H_2O$  in alk. soln. by a slow stream of air in the presence of  $Ce(OH)_4$  or  $Fe(OH)_3$  within 5-5 hrs. In some cases complete oxidation is attained only with increased amts. of alkali. The results are given in tables and application is made to diabetes. J. T. S

The prosthetic group of the blood pigment (KCTER, HEGS) 10. An amino acid of the indole series from casein (AUBERHALDEN, SICKEL) 10.

OPPENHEIMER, CARL and KUTH, RICHARD: Fermente und Ihre Wirkungen Pts. (V), (VI), (VII). Leipzig. Georg Thieme. Price V, R. M. 10 20, VI, 10 50; VII, 12 00. Cf C A 19, 1719

## B—METHODS AND APPARATUS

STANLEY R. BENEDICT

Surface tension of liquids met with in biochemistry, with special reference to brewery worts. J. KING. *J. Inst. Brew.* 31, 32-7 (1925).—The advantages and disadvantages of the different methods for measuring surface tension are discussed. A method giving reasonably good results has been devised based on the same principles as that of Morgan, Harkins and Brown. An app. is described in which the rate of drop formation is controlled by gravity flow through a capillary tube. The drop is made to form quickly by means of air pressure, which is released 30-60 secs. before each drop is sufficiently large to drop by gravity. The drops are caught in a weighed bottle immersed in a water bath. The time taken to form a drop can be controlled by the height of the head of liquid above the capillary and the length and bore of the latter. These are so chosen that the period of 5 min. can easily be obtained in any liquid likely to be used with a particular capillary tip. The surface tension of worts of gravities from 1011 to 1179 was detd. by the above method. It varied from 54 to 41 dynes/cm. with increasing concn. When these values are plotted against concn., a curve similar to that of substances exhibiting the phenomenon of positive surface tension is obtained. The surface tension of sugar solns. varied between 50 and 65 dynes/cm., while dextrin soln. gave a value of 57.8. Thus the main constituents of wort are not to any great extent responsible for the lowering of surface tension, which in worts is due to small quantities of substances exhibiting surface tension to a high degree. B. C. A.

Determination of the free acid of gastric juice. H. SAHLI. *Schweiz. med. Wochschr.* 54, 1-6 (1924).—An aq. soln. of an indicator is titrated with 0.1 N HCl until the color matches that obtained with gastric juice contg. the same indicator. For acid juices and for less acid juices, the indicators used are methyl violet and litmus, resp. B. C. A.

The oxygen-binding capacity of blood pigments with the ferricyanide method. S. MASUDA. *Biochem. Z.* 156, 21-34 (1925).—Low results were obtained with Barcroft's differential app. for the detn. of O content of blood. This was due to the binding of a part of the blood O by unknown compds. formed in the presence of the  $NH_3$  used in this method.  $CO_2$  may contribute to the gas pressure measured as O and contribute another error. Barcroft's method is not regarded as accurate enough for physiol. investigations involving O detns. in the blood. F. A. CAJONI

The determination of phosphoric acid in metabolism experiments. C. SCHWITT-KRAEMER. *Biochem. Z.* 156, 40-50 (1925).—Of various methods for the detn. of  $H_3PO_4$  in biological material, that were tried Neumanns (*Z. physiol. Chem.* 43, 35 (1904)), was found the most valuable. F. A. CAJONI

Comparison of the determination of urea in human and animal urines. K. KIKUCHI *Biochem. Z.* 156, 35-9(1925).—The gravimetric procedure for urea detn involving xanthidrol gave accurate results in human and animal urines. Equally valuable results were obtained from the method of Folin. Urease methods gave low results. The gasometric (hypohromite) methods were found to be very inaccurate.

F. A. CAJORI

The quinhydrone electrode in clinical  $p_H$  measurements. R. SCHAEFER AND F. SCHMIDT. *Biochem. Z.* 156, 63-79(1925).—Expts indicate that the quinhydrone electrode is applicable for the detn of  $p_H$  in such clinical material as gastric contents, urine and cerebrospinal fluid.

F. A. CAJORI

The determination of the odor threshold. F. HOFMANN AND A. KOHLRAUSCH. *Biochem. Z.* 156, 287-94(1925).—An app. is described whereby different mixts. of an odorous substance and air are blown to the nose of the subject until the threshold for odor is reached. The results are expressed in terms of vapor pressure of the substance being tested.

F. A. CAJORI

Experiences with a new hemoglobinometer. K. BÜRKE. *Biochem. Z.* 156, 379-80(1925).—An accuracy of 1% is obtained with the author's app. and method which was described elsewhere (*C. A.* 18, 2354).

F. A. C.

Significance of the reaction of Utz. G. B. ZANDA. *Biochem. therap. sper.* 10, (1923); *Arch. ital. biol.* 74, 84(1924).—Utz's reagent, alk. soln. of phenolphthalein decolorized with Zn, is a delicate test for Cu. Since Cu is normally present in tissues the rosy color given with blood and tissues is not a sp. test for blood but for Cu.

A. T. CAMERON

Method for the separate determination of potassium and sodium in urine. O. V. DERN. *Z. physiol. Chem.* 144, 178-80(1925).—The method of Kramer and Tisdall (*C. A.* 15, 1912, 2461) for Na and K in serum does not give satisfactory results when applied to urine. The following method is claimed to avoid the objectional features. Heat 20-30 cc. of urine with an equal amt. of concd.  $HNO_3$  in a Kjeldahl flask 10-2 hrs. on the water bath, then add 1 or 2 glass beads and evap. on an asbestos plate over a small flame. If C particles remain repeat the  $HNO_3$  treatment. If the urine contains much protein the latter should first be coagulated and filtered, and the ashing performed with an aliquot of the filtrate. After cooling evap. the residue several times with HCl until the ash is white. Dissolve the residue in 0.1 N HCl, transfer to a volumetric flask and dil. to the original vol. of the sample. Unless Fe is present from blood contained in the urine, the soln. is now colorless. Ppt. the Ca and Mg (cf. Kramer and Tisdall), transfer the filtrate to a glass dish, add KOH and phenolsulfonephthalein, place a filter paper moistened with this indicator over the dish and heat on the water bath until the paper shows neutral reaction (expulsion of  $NH_3$ ). Ppt. Na with  $K_2H_2Sb_2O_7$ . The limits of error are 1.5-2%. [K detn. is not described. AASTA.]

A. W. DOX

Investigation of tryptic digestion mixtures with the colorimetric method for the determination of amino acids according to Folin. J. ELLINGHAUS. *Z. physiol. Chem.* 145, 40-4(1925).—Comparative detns. of  $NH_2$  acids by the van Slyke, Sorensen and Folin methods in the digestion mixts. obtained from casein + pancreatin, casein +  $H_2SO_4$ , fibrin + pancreatin, and casein + pepsin + erepsin gave values in close agreement. The advantage of the Folin method is the very small amt. of substance required for the detn.

A. W. DOX

Gas narcosis. H. W. KNIPPING. *Z. physiol. Chem.* 145, 144-53(1925); cf. *C. A.* 18, 3100.—Description of an app. for administering gas mixts. for anesthesia, whereby loss of gas is avoided by the use of a closed system and the mixt. is subject to automatic control.

A. W. DOX

Technic of the study of gas metabolism. H. W. KNIPPING. *Z. physiol. Chem.* 145, 151-76(1925); cf. *C. A.* 18, 3402.—Description of app. and details of manipulation.

A. W. DOX

Non-specificity of reactions to indophenol and benzidine of so-called oxidase cell granules. HOLLAND. *Bull. histol. appl. physiol. path.* 1, 421-40(1924); *Physiol. Abstracts* 9, 573.—Criticism from the chem. point of view of methods for detecting oxidase ferments in cells. Granules considered as oxidases are not specific. H. G.

The value of histological reactions of oxidases. MARCEL PRENANT. *Bull. histol. appl. physiol. path.* 1, 499-508(1924); *Physiol. Abstracts* 9, 573.—No biochem. value may be credited to methods by which histologists claim to find oxidases in cells. Work relying on these methods, and conclusions drawn from them, should be thoroughly revised.

H. G.

Micro-method of urea estimation. GRIFOLS Y ROIG AND KURT HELMHOLZ. *Deut. med. Wochschr.* 36, 1217(1924); *Physiol. Abstracts* 9, 503.—Urea in blood serum,

urine, and cerebrospinal fluid may be estd. by the use of permittite. The urea is decomposed by urease, and the resulting  $\text{NH}_3$  is absorbed by permittite, which is washed and treated with  $\text{NaOH}$ . The soln. is then nesslerized. H. G.

The determination of the salt error of indicators and the accurate estimation of the  $p_H$  of solutions by colorimetric methods. J. T. SANDERS. *Proc. Camb. Phil. Soc. (Biol.)* 1, 30-48(1924); *Physiol. Abstracts* 9, 568.—It is shown that under certain conditions differences of  $p_H$  0.02 can be detected with Clark's and Lub's sulfonephthalein indicators. Curves are obtained relating the salt error of cresol red with the logarithm of the normality, so that in any given case the discrepancy due to this cause can be allowed for. In this way, by taking advantage of the overlap of other indicators with cresol red, their salt errors can also be detd. The application of these facts to work with sea water is discussed. H. G.

The interfering effect of glycerol on the biuret reaction. FLORENCE B. SEIBERT AND E. R. LONG. *J. Biol. Chem.* 64, 229-31(1925).—"Glycerol interferes markedly with the delicacy of the biuret test, presumably through its combining power for  $\text{Cu}(\text{OH})_2$ . As small a quantity as 0.33% prevents the reaction in solns. of casein and gliadin of 1-9600 concn., and in solns. of tuberculin protein of 1:4800 concn., the limiting concns. at which these proteins give a positive biuret in the absence of glycerol.  $\text{NH}_4$  citrate in concns. corresponding to those used in culture media does not inhibit the development of the biuret color." I. GREENWALD

A micro-method for determining nitrogen. A. R. ROSE. *J. Biol. Chem.* 64, 253-6(1925).—The modification consists of the use of a special tapered digestion tube, a mixt. of  $\text{H}_2\text{SO}_4$ ,  $\text{HClO}_4$  and  $\text{H}_2\text{O}_2$  for digestion and direct nesslerization. Good results are claimed for urine, serum, blood, etc., but low results were obtained with creatinine and guanidine. I. GREENWALD

Detection of sugar in urine in the presence of santonine. G. PÉOTIER. *Ann. chim. anal. chim. appl.* 7, 66-7(1925).—Santonine is sometimes prescribed in the treatment of diabetics. As a result the urine assumes a strong yellow color and the detection of sugar is made more difficult. Often a red coloration is obtained instead of pptn. of  $\text{Cu}_2\text{O}$  after treatment with Fehling soln. Santonic acid prevents the pptn. By adding  $\text{AcOH}$  dropwise the pink color changes to yellow and then  $\text{Cu}_2\text{O}$  will ppt. W. T. H.

Test for wroblin and the determination of chloride in blood. REOHLON. *Ann. chim. anal. chim. appl.* 7, 131(1925).—Criticism of the paper by Beaugerel (*C. A.* 19, 1873). W. T. H.

Biological analyses. MULLÉRE. *Ann. chim. anal. chim. appl.* 7, 131-4(1925).—In the analysis of urine the chemist does not always give results which are easily interpreted by the physician. Some suggestions are made which should be helpful both to the chemist and to the physician. W. T. H.

Isolation of methylguanidine from the urine in two cases of parathyroid tetany. E. FRANK AND J. KCHENAT. *Klin. Wochschr.* 4, 1170-1(1925).—A mixture of methyl- and dimethylguanidine was isolated from the urines of 2 cases as picrate (Fridlay-Sharp) and as carbonate (Kutscher Lohmann). Case 1:1500 cc. of urine gave 0.93 g. picrate. Case 2: 2000 cc. of urine gave 1.432 g. picrate. Guanidine (methyl- or dimethyl-) picrate could not be obtained from normal urine. The method is not described. MILTON HANKE

A new blood reaction or improvement of the Abderhalden reaction? W. WITTKOP. *Klin. Wochschr.* 4, 1214(1925).—A discussion of the work of Sellheim (*cl. C. A.* 19, 2079) in which W. shows that Sellheim's reaction is not new but is merely an improvement. MILTON HANKE

New method for studying pure gastric secretion. A. I. GARRAT. *Am. J. Med. Sci.* 169, 687-91(1925).—A duodenal tube is introduced into the duodenum and a second tube into the stomach. Following duodenal feeding gastric secretion takes place almost immediately, the juice secreted being readily collected for examn. without admixt. with test meals. G. H. S.

Some laboratory apparatus and methods for embryological and cytological work. J. A. LONG. *Anat. Record* 29, 318-40(1925).—Among the technical procedures described those of chem. interest are: a method of ripening hematoxylin, keeping osmic acid solns. and mixts., app. for the gradual mixing of fluids, device for facilitating tissue infiltration with paraffin and methods for working with wax plates. G. H. S.

Determination of CO by the blood method (NICKOLUX) 7.

## C—BACTERIOLOGY

A. K. BALLS

Fermentation of oxalacetic acid. C. NEUBERG AND G. GORR. *Biochem. Z.* 154, 495-502(1924).—Acetoin, isolated as its *p*-nitrophenylhydrazone, m. 304, malic acid and  $\alpha,\beta$ -butylene glycol were isolated from the yeast fermentation of oxalacetic acid. The yield of acetoin was 15%.

F. A. CAJORI

The esterification of phosphoric acid by yeast. A. GOTTSCHALK AND C. NEUBERG. *Biochem. Z.* 154, 292-4(1924).—If coenzyme from bottom yeast is added to acetone yeast prep'd from top yeast, a 100% esterification of  $H_3PO_4$  occurs in the presence of glucose. A 50 to 60% esterification results from addition of coenzyme from rabbit muscle.

F. A. CAJORI

The photochemical reduction of  $\alpha,\alpha,\beta$ -trichlorobutyraldehyde to 2,2,3-trichlorobutanol. L. ROSENFELD. *Biochem. Z.* 156, 54-7(1925).—Trichlorobutyl alcohol (I) was obtained by distn. from an actively fermenting yeast culture in cane sugar to which trichlorobutyraldehyde hydrate had been added. After redistn. and recrystn., snow-white crystals of I were obtained, m. 61-62,  $[\alpha]_D^{25}$  2.5.

F. A. CAJORI

Dried yeast. HARRY SODOTKA. *Z. physiol. Chem.* 145, 91-4(1925); cf. C. A. 18, 2538.—Zymase is not partially but wholly bound by the plasma and is liberated in the prep'n. of cell-free juice but not by mere dehydration of the cells. There is thus no fundamental difference between fermentation by fresh and by dried yeast. Euler's comparison of the inhibitory effect of  $PhOH$  has not taken into account the difference in amt. of dry substance and consequently the difference in concn. of the poison.

A. W. DOX

Biological investigation of the bile acids. I. Cleavage of cholic acid by *Bacterium coli commune*. KOZOO KAZIRO. *Z. physiol. Chem.* 145, 227-37(1925).—By growing *B. coli commune* on a culture medium contg. inorg. salts, glycerol and cholic acid, a cryst. substance  $C_{27}H_{45}O_6$ , m. 183-4°,  $[\alpha]_D^{20}$  40.086°, was obtained. The substance is insol. in alkali and probably results from splitting off of the side chain,  $C_8H_{15}COOH$ , from cholic acid. Oxidation with  $CrO_3$  converts it into a dehydro comp'd.  $C_{27}H_{43}O_6$ , m. 150-1°, which gives a permanent yellow color with  $Ac_2O$  and  $H_2SO_4$ .

A. W. D.

The cleavage of carnosine by intestinal bacteria and its relation to autointoxication of the organism. JULIE HERTER. *Z. physiol. Chem.* 145, 276-89(1925).—Carnosine ( $\beta$ -alanylhistidine) is more difficultly broken down by bacterial action than histidine. Cultures obtained from a large no. of feces from normal and sick persons behave differently toward carnosine and histidine in culture media. All the organisms which decomp. carnosine attack histidine also, whereas a large no. decomp. histidine completely but leave carnosine intact. *Bac. pyocyaneus* readily attacks both, the end products from carnosine being  $NH_3$ ,  $AcOH$ ,  $PrCO_2H$ , etc., none of which is toxic. The biol. significance of these observations is the fact that carnosine, which may comprise as much as 0.4% of the meat used for food, is not converted by intestinal bacteria into histidine and thence into the powerful drug histamine, but is either broken down completely or not at all.

A. W. DOX

Two new microbes which decompose starch. A. S. SEDICH. *Russian Health Resort Service* No. 1, 11-7(1923).—S. claims to have isolated 2 microbes from the soil: one a spore-forming rod, and the other a coccus. The former decomposes starch to dextrin and no further, the other up to the sugars, which are utilized and decomposed after all the starch has been used. These organisms do not decompose cellulose. The first form does not develop on  $EtOH$ , glycerol or mannitol.

J. S. JOFFE

Assimilation of hydrocarbons by bacteria of the Tambookansk and Petrovsk muds in reference to mud formation. V. M. GOBIN. *Russian Health-Resort Service* No. 5, 3-9(1923).—To det. whether bacteria capable of assimilating hydrocarbons exist in muds, the Beijerinck medium was used. A rod-shaped organism, non-spore former, developed and was named *Bacterium hidum*. Ethane could be replaced with benzene or coal oil. The ethane is oxidized to  $CO_2$  and  $H_2O$  with the formation of intermediate products.

J. S. JOFFE

Microbic respiration. I. The compensation manometer and other means for the study of microbial respiration. F. G. NOVY, R. H. ROHM AND M. H. SOULE. *J. Infectious Diseases* 36, 109-87(1925). II. Respiration of the tubercle bacillus. F. G. NOVY AND M. H. SOULE. *Ibid* 168-232.—This is a study of a single strain of human tubercle bacillus grown on certain solid media. By the use of exact method, the gas changes of the organism were followed under varied conditions, its av. corrected real respiratory quotient, when grown on glycerol agar, was 0.836; on glucose agar, 0.992; while on rabbit serum agar, it was 0.904. The quotient was not influenced by the growth

of the organism in high or low  $O_2$  or in high  $CO_2$  tensions. The theoretical value is, for glycerol, 0.857, for glucose, 1. The analyses demonstrated that the gas exchange was greatest when the organism was grown on glycerol agar. A good growth was obtained on glucose agar. In order to obtain a rich growth in a single tube, about 100-150 cc of  $O$  must be provided. This means a supply of ordinary air corresponding roughly to 500-700 cc at  $37^\circ$  and 750 mm. The analyses also demonstrate that the yield of  $CO_2$  was slightly less than the amt. of  $O$  consumed. In tests with air, in jars, as much as 150 cc of unreduced  $CO_2$  were produced by a single culture. In a closed, ordinary culture tube the  $O$  was removed in a few days by the inoculum, and no visible growth resulted. A very slow growth, or none, in tubes closed either in the flame, or with sealing wax, paraffin, or rubber stoppers means an insufficient supply of  $O$ . When all of the  $O$  (20.9%) was consumed by the culture, the total  $CO_2$  yield reached about 17.5%. This does not mean  $O$  retention by the cell. It merely expresses the fact that in the combustion of glycerol the vol. of  $CO_2$  produced is less than the vol. of  $O$  consumed, as expressed by the ratio 6/7 and, hence, by the quotient 0.857. One-seventh of the  $O$  consumed combines with  $H_2$  to form  $H_2O$  and, as a result, a corresponding negative pressure develops. When glycerol agar is used as the culture medium, the manometer developed a negative pressure which reached a const. level as soon as the  $O$  was entirely consumed. Some of this negative pressure was due to loss of  $CO_2$  by soln. in the medium. There was an additional loss of  $CO_2$  when rubber stoppers were used. Rich cultures developed in tubes which were attached to manometers, provided that they were evacuated and refilled with pure air as often and as soon as  $O$  removal was indicated. After 5-10 refills, the  $O$  thus supplied was enough to provide a good growth. The vol. of growth was strictly proportional to the amt. of  $O$  consumed, provided the  $O$  tension was const. When such tubes were refilled so as to contain increasing tensions of  $O$ , the manometers responded with increased negative pressures, and the analyses showed corresponding high yields of  $CO_2$ . Thus, a tube charged with slightly less than 100%  $O$  showed a pressure of -162 mm and yielded 86% of  $CO_2$ . The optimal concn. of  $O$  was about 40-50%. Above that limit, growth was less abundant. In 100%  $O$ , the growth developed as isolated, thick, moist, white colonies; at the end of 58 days, such a culture was infective. Growth occurred when the  $O$  tension was decreased below that in air. In atm. contg. 10, 6, 3, 1 and 0.5%  $O$ , the rate of growth was correspondingly retarded. An essential condition for good growth under diminished tension is that the vessel shall contain at least 100 cc. of  $O$ . Growth continues "until the last atom" of  $O$  is consumed. With a like consumption of  $O$  (100 cc.), the growth mass is proportional to the  $O$  tension originally present in the container. The higher the tension (up to certain limits), the greater is the growth mass. The lower the tension, the smaller and poorer is the growth. In atm. contg. 10 to 50% of  $CO_2$  the growth of the tubercle bacillus was not inhibited. In concns. of 60% or more there was some inhibition, but fair growth was obtained in 90%  $CO_2$ . The growth which developed in 85-98%  $CO_2$  for 59 days was viable and infective. The tubercle bacillus as it grows produces  $CO_2$  but the removal of this  $CO_2$  as fast as it is produced does not stop growth. Whatever growth inhibition occurs when a culture is kept over alkali is the result of desiccation of the surface of the medium. Moisture sufficient to wet the surface of the medium was found to be an important factor in securing rich and even growths. The vapor tension of  $Hg$  was sufficient to inhibit the growth under ordinary  $O$  tension. Under high  $O$  tension the organism multiplied in the presence of  $Hg$  vapor, but the resultant growth was grayish black and infective. The best results as regards rapidity of growth and richness of culture were obtained with a meat-ext. medium contg. 1% agar and 5% glycerol. Moisture can be supplied by a fine jet of steam introduced into the cotton plug. After inoculation such tubes were closed with sealing wax and holed by means of a hot Pt. needle. This method of cultivation and sealing is recommended, since in from 7 to 10 days it gave good growths. The slow multiplication of the tubercle bacillus in the body is explainable from the standpoint of growth in diminished  $O$  tension. An indefinite supply of  $O$  under a tension corresponding to a few mm. of  $Hg$  will probably enable the organism to grow, although very slowly. The "rest cure" and rich diet in checking the progress of the disease probably act by reducing to a min. the available  $O$  supply in the tissues.

JULIAN H. LEWIS

The course of growth of *Bacillus proteus vulgaris* in relationship to several digestive products. ROSSI MELLER. *Centr. Bakt. Parasitenk., II Abt.* 64, 1-32 (1925). — An antiproteolytic enzyme was found. Many growth curves are given. J. T. M.

A nitrite-forming bacterium. J. SACK. *Centr. Bakt. Parasitenk., II Abt.* 64, 32-40 (1925). — *Nitrobacter floriss oxidizes*  $NH_3$  to nitrite and then nitrate. J. T. M.

The darkening of *Azotobacter chroococcum* Beij. by melanin formation. AUGUST

RAPPEL AND OSCAR LUDWIG. *Centr. Bakt. Parasitenk., II Abt.* 64, 161-6(1925).—Young colonies of *Azotobacter* are colorless. They later turn brown and then almost jet black as a result of the oxidation of tyrosine to melanin. This is the first instance of such a process being carried out by bacteria. JOHN T. MYERS

The metabolism of urea-splitting bacteria at a temperature below 0°. L. RUBENTSCHIK. *Centr. Bakt. Parasitenk., II Abt.* 64, 160-74(1925).—One organism is given the name "urea bacillus psychrocarcticus" and another is called "urea sarcina psychrocarctica," because they continue to grow and to split urea at a temp. of  $-1.25^{\circ}$  to  $-2.50^{\circ}$ . JOHN T. MYERS

Studies on the food sources of carbon and nitrogen for several molds. H. H. HOCHAPPEL. *Centr. Bakt. Parasitenk., II Abt.* 64, 171-222(1925).—Four molds were studied. The optimum  $pH$  was 4.3-5.5 and the optimum temp. 26-28°. Growth occurred in the presence of 60% dextrose or sucrose. Cultures increase in alk. in the presence of all sources of C except dextrin, lactose and arabinose. Org. acids were unsatisfactory. Chem. inert substances were best. Atm. N was not utilized, and nitrite only in alk. soln. nitrate and  $NH_3$  were fairly good sources of N.  $Cl_2$ ,  $SO_4$ , oxalate and acetate salts of  $NH_3$  were unfavorable.  $NH_4$ , succinate, glycocoll, and bactopectone furnished both C and N.  $NaNO_3$ ,  $KNO_3$ , and  $NH_4NO_3$  were fairly good sources of N. They produced a urea-splitting enzyme.  $ZnSO_4$  increases the economy of growth. Growth is less economical with dextrose than with other carbohydrates. JOHN T. MYERS

Appropriate directions for the preparation of silicic acid culture media and several contributions to the physiology of aerobic cellulose-dissolving bacteria. RUDOLPH BOJANOVSKY. *Centr. Bakt. Parasitenk., II Abt.* 64, 222-32(1925). JOHN T. MYERS

Contributions to the knowledge of bacterial enzymes (catalase and peroxidase). C. STAPP. *Centr. Bakt. Parasitenk., I Abt. Orig.* 92, 161-93(1924).—Catalase was detected in 10-year-old dry cultures of *Streptococcus apis*, *B. coli*, *B. fluorescens* and *Vibrio* Dunbar, but not in the organism of the crab pest. The method of drying influenced the stability of the catalase. When the culture was extd. with  $CHCl_3$  and acetone and dried the catalase was destroyed, but not when it was dried over  $H_2SO_4$ , even when kept at room temp. Such salts as  $KNO_3$ ,  $K_2SO_4$ , and  $KClO_3$  did not all exert the same influence on catalase production.  $KNO_3$  increased it. Bubbling such gases as  $H_2$ ,  $N$  or  $O$  for 1 or 2 hrs. prior to the addn. of  $H_2O_2$  had no influence on the activity of the catalase. Heating cultures of non-spore formers to  $80^{\circ}$  for 15 min. inactivated the catalase, but spore formers withstood a temp. of  $100^{\circ}$ . Anaerobes produced less catalase than aerobes. For *B. prodigiosus*, *Staphylococcus albus* and *Staph. aureus*, the min. H-ion concn. for catalase activity was 9.1, the optimum between 8.0 and 6.5, and the max. 3.1. Treatment with strong  $HCl$  followed by neutralization with  $NaOH$  or vice versa effected different species differently.  $CHCl_3$  and acetone slowly weakened the catalase. 0.003% I inactivated catalase in 1 hr.;  $CS_2$  checked its activity, but to different degrees with different bacteria. Peroxidase was formed by all bacteria except streptococci. In contradistinction to catalase it is indifferent to neutral salts, acids, alkalies, I,  $CS_2$ ,  $C_6H_6$ , toluene, xylene, alc., and narcotics. JOHN T. MYERS

Bacterial and yeast antagonism. III. IGNAZ SCHILLER. *Centr. Bakt. Parasitenk., I Abt. Orig.* 94, 64-6(1925); cf. C. A. 18, 3620.—Many bacteria produce a lytic substance for the yeasts of beer and wine. It does not coagulate blood serum or egg white. JOHN T. MYERS

Chromogenic bacteria in eggs. ADOLPH SEISER. *Centr. Bakt. Parasitenk., I Abt. Orig.* 94, 74-7(1925). JOHN T. MYERS

The sugar content of culture media. WILHELM ROTHER. *Centr. Bakt. Parasitenk., I Abt. Orig.* 94, 77-80(1925).—Infusions of placenta have a lower sugar content than those from horse muscle. The reaction of placenta infusion is alk. to litmus and acid to phenolphthalein. JOHN T. MYERS

Growth-stimulating properties of filtrates of tubercle bacillus cultures and of other substances. HANS SCHMIDT. *Centr. Bakt. Parasitenk., I Abt. Orig.* 94, 94-9(1925).—Filtrates from tubercle bacillus cultures increase the rate of growth of fresh cultures. Heating the filtrates for 1 hour at 100 only slightly decreases the effect. 0.1 to 0.001%  $FeCl_3$  stimulates growth. JOHN T. MYERS

The ectoplasm of bacteria. II. The color differences between Gram-negative and Gram-positive bacteria. A contribution to the theory of the Gram stain. M. GUTSTEIN. *Centr. Bakt. Parasitenk., I Abt. Orig.* 94, 145-51(1925).—The difference between Gram-positive and Gram-negative organisms resides in the ectoplasm. A Gram-positive organism becomes negative when the ectoplasm can no longer be demonstrated by 5% tannic acid. JOHN T. MYERS

A growth stimulant for the Koch-Weeks bacillus and its relationship to Pfeiffer's influenza bacillus. III. Solubility and adsorption of the growth-promoting substance of the red corpuscles. MAXIMILIAN KNORR. *Centr. Bakt. Parasitenk., J. Abt. Orig.* 94, 161-5(1925).—The "V" body is as important for growth as the "X" body.

JOHN T. MYERS

The disinfecting power of raw chloramine "Heyden" on tuberculous sputum. WALTHER BRUNK. *Centr. Bakt. Parasitenk., J. Abt. Orig.* 94, 236-7(1925).—Tubercle bacilli were killed in 4 hours in dry sputum by a 4% concn. and in moist sputum by a 27% concn.

JOHN T. MYERS

Intestinal infections of rodents with the bacillus of Danysz and Moreshkowsky. J. H. PETROFF. *Centr. Bakt. Parasitenk., J. Abt. Orig.* 94, 265-9(1925).—These organisms are very sensitive to HCl, being killed in 35 to 40 min. by a concn. of 0.02%. The addn. of 1% starch or peptone does not lower the lethal effect. One % mucus lowers the lethal effect 8 to 10 times.

JOHN T. MYERS

The influence of different dyes on bacterial growth. ERNST OESTERLIN. *Centr. Bakt. Parasitenk., J. Abt. Orig.* 94, 313-20(1925).—Gentian violet, crystal violet, malachite green, aniline violet and safranin in bouillon, agar, or gelatin showed a selective inhibition of the growth of Gram-positive bacteria. They were less effective in a liquid than a solid medium. The same result occurs in salt soln. suspensions if heated to 45° for 1 hour. Acid fuchsin and other dyes had no selective effect on Gram negative organisms. Aniline violet and safranin would not kill spores.

JOHN T. MYERS

Cultivation of the Koch-Weeks bacillus. IV. Histidine hydrochloride media for the cultivation of hemophylic bacilli. MAXIMILIAN KNORR AND WALTER GEHLEN. *Centr. Bakt. Parasitenk., J. Abt. Orig.* 94, 321-6(1925).—The value of adding 0.1-0.2% of histidine-HCl to hemophylic media was not confirmed.

JOHN T. MYERS

The volatility of the bacteriophage lysin. ALBRECHT GERCKE. *Centr. Bakt. Parasitenk., J. Abt. Orig.* 94, 387-96(1925).—No evidence was found that the lysin was volatile.

JOHN T. MYERS

Color separation of bacteria by means of the Victoria-blue-pyronine method. JOSEF SCHUMACHER. *Centr. Bakt. Parasitenk., J. Abt. Orig.* 94, 397-400(1925).—There is more detail than by the standard Gram method. Use the following technic. Twenty-five percent tannic acid for one minute in the cold. Heat with glycerol victoria blue for 30 sec. (Add 2 g victoria blue to 50 cc. alc. Let stand overnight and add 50 cc. of 4% phenol. Dil. 10 times for use.) Remove as much color as possible with phosphine alc (0.2 g. "phosphine," chrysianiline extra, not phosphine R, in 100 cc. of absolute alc.) Cover with 1% pyronine or safranin for 10-15 sec.

JOHN T. MYERS

A new culture medium for spirochaetes Obermeieri. W. ARISTOWSKY. *Centr. Bakt. Parasitenk., J. Abt. Orig.* 94, 445-52(1925).

JOHN T. MYERS

Studies on the metabolism of *B. botulinus* in various media. XXVI. E. WAGNER, K. F. MEYER AND C. C. DOZIER. *J. Bact.* 10, 321-412(1925).—*B. botulinus* induces in a 2% peptone soln. a slow evolution of gas, and a slow accumulation of  $\text{NH}_3$ , amino and volatile acids with little change in reaction. The addn. of glucose increases the metabolic activity of the organism, but may decrease the potency of the toxin. The addn. of gelatin to peptone soln. increases its nutritional but not its buffer value. Albumoses and proteoses are not necessary for growth or toxin formation. The N fractions of various commercial peptones varies. Toxin production is intimately connected with proteolytic activity, which is favored by the exclusion of O. The volatile acids in a 10-day-old meat culture consist of valeric, butyric, and acetic in the ratio of 3:7:2. Old and recently isolated cultures of *B. botulinus*, *B. sporogenes* and *B. histolyticus* have similar biochem. activities. *Vibrio septique* causes only a slight degradation of N constituents of the medium. *B. tetani* produces profound chem. changes in meat media. Twenty-one hrs' fermentation of a medium with *B. welchii* decreases its value for the growth of *B. botulinus*. Milk possesses only a moderate biologic value for *B. botulinus*. Cultures contain both casein-coagulating and casein-digesting enzymes. The addn. of 1.25% glucose to milk increases the gas production and the H-ion concn., and decreases the production of  $\text{NH}_3$ ; but has no effect on the production of amino or volatile acids. A soln. of casein digest having approximately the same total N content as whole milk has a high biologic value for *B. botulinus* and *B. tetani*. *B. botulinus* produces a larger amt. of volatile acids of higher mol. weight than does *B. tetani*.

J. T. M.

Variations of the agglutinating power of an immune serum mixture under the influence of the continuous current. J. CLUZET, A. ROCHAUX AND TH. KOFMAN. *Compt. rend.* 180, 1611-3(1925); cf. *C. A.* 19, 1582.—Notwithstanding the prolonged passage of the d. c. the 2 bacilli tested retain their specific agglutinating powers.

L. W. RIGGS

Induced antiseptics or germicidal action at a distance without material contact on a bacterial dilution by a very dilute solution of sodium hypochlorite. PHILIPPE BUNAU-VARILLA AND EMILE TECHOUEVRES. *Compt. rend.* 180, 1615-8(1925).—Expts. to test the action of very dil. solns. of NaClO on the org. matter of drinking water led to the following hypothesis: The mols. of NaClO in attacking org. matter apparently emit rays which act on microorganisms in a manner similar to that of the ultra-violet rays, creating around the focus of chem. action a zone of destruction of these forms of life. In 60 tests, 51 confirmed this hypothesis. In a second series of 17 tests 16 confirmed this hypothesis. L. W. RIGGS

Presence of argon in gases evolved during the alcoholic fermentation of glucose. AMÉ PICTET, WERNER SCHERRER AND LOUIS HELFER. *Compt. rend.* 180, 1629-32 (1925).—Fermentation of 200 g. of glucose and 200 g. of moist yeast was allowed to take place for 48 hrs. in a vessel from which the air had been swept out by a current of CO<sub>2</sub>. After the fermentation the resulting gas in the app. was deprived of CO<sub>2</sub> by means of a KOH soln. and the remainder analyzed giving N 70.2%, O 27.2, A 2.6. The expt. was repeated with care to eliminate the air in the water used in making the various solns. The result proved that the A found was a product of fermentation. L. W. RIGGS

Retardation of the action of oxidases by bacteria. IRVING KUSHNER AND A. S. CHAIKELIS. *Science* 62, 36-7(1925).—After milk has reached a certain degree of staleness it fails to oxidize a guaiac soln. to give a blue color. This failure is due to the no. of bacteria present. Up to about 3 millions of bacteria per cc., the action of the oxidases is accelerated. An increase in the no. of bacteria beyond this figure retards the action of the oxidases. L. W. RIGGS

The oxalic acid test for indole. S. A. KOSER AND R. H. GALT. *Abstr. Bacteriology* 9, 6(1925).—A pink color forms when volatile indole comes in contact with oxalic acid paper held in the mouth of the culture tube. Delicacy of the test is influenced by reaction of the medium. This test was compared with the Salkowski's, Ehrlich's, the vanillin and Gore's modification of the Ehrlich tests. The oxalic acid test has advantages over other tests in that the culture is not destroyed when a test is made. F. W. TANNER

Destruction of cellulose by aerobic bacteria (GROENEWEGE) 23. Annual report of the agricultural chemist to government, Punjab (LANDER) 15.

## D—BOTANY

B. M. DUGGAR

Spectrum of chlorophyll in the living leaf. J. WLODEK. *Bull. Internat. Acad. Pol. Sci. Lettres* 1924B, 407-23.—The displacement of the chlorophyll spectrum of the living leaf towards the infra-red region in comparison with that of a soln. of chlorophyll appears to be attributable to the optical system of the tissue of the leaf, as also is the effacement of the boundaries of the absorption bands. The spectrum of the leaf chlorophyll is probably a mixed spectrum composed of a common with a reflected spectrum intermixed with unabsorbed light. The duality of the first absorption band of chlorophyll, observed with both the living and the killed leaf, is explainable by assuming that the spectrum of the chlorophyll is not that of a mixt. of green pigments, but is composed of 2 distinct superposed spectra of neo- and allo- (a- and b-) chlorophylls. Under the influence of light, the spectra of leaf chlorophyll undergo change; the stripes of the first absorption band corresponding with both chlorophylls alter in width, thus indicating either a change in the relative amts. of the 2 chlorophylls or the appearance of new spectra of unstable compds. of chlorophyll with CO<sub>2</sub>. B. C. A.

Blackening of Orobanches in the course of their desiccation. M. BRIDEL AND C. CHARAUX. *Compt. rend.* 180, 387-8(1925).—The blackening which occurs during drying of the plants is attributed to enzymic oxidation, without hydrolysis, of their special glucoside, now named orobanchoside (cf. C. A. 18, 3075). Also in *Bull. soc. chim. biol.* 7, 474-85. B. C. A.

Joseph Vallot (1854-1925). E. A. MARTEL. *La nature* 53, i, 367-8(1925).—An obituary with portrait. C. C. DAVIS

The occurrence of gitogenin in digitalis leaves. A. WINDAUS AND J. BRUNKEN. *Z. physiol. Chem.* 145, 37-9(1925).—A by-product from E. Merck obtained in the prepn. of digitalis glucosides was found to be gitogenin (C. A. 8, 96) and identified by means of m. p., analysis, and diacetyl, dipropionyl and dibenzoyl derivs. It probably results from the action of a sp. enzyme. A. W. DOX

The chemical constituents of malt rootlets with special reference to hordenine. YOSHITAKA HASHITANI *J. Coll. Agr. Hokkaido Imp. Univ.* 14, 1-56(1924).—The cell walls of malt rootlets consist chiefly of cellulose and hemicellulose with some lignin. Glucose, fructose, xylose and possibly galactose were detected in the hydrolytic products of the cell wall. Glucose and fructose were found in the malt rootlets. The ash of the rootlets consists chiefly of  $P_2O_5$  and  $K_2O$ . The nitrogenous substances consist chiefly of proteins, sol in 0.25% NaOH and 10% NaCl, amino acids and purine bases. Asparagine, adenine, choline, betaine and hordenine also were isolated. The following derivatives of hordenine were prepared: hydrochloride, hydrobromide, acid tartrate, neutral tartrate, methiodide, ethiodide, acetylhordenine, benzoylhordenine and hydrobromide, trimethyl sulfate, bromide and sulfate. Hordenine was found widely distributed in seedlings of the Gramineae. Hordenine is attacked by tyrosinase of barley, malt and malt rootlets but not by urease, catalase, oxidase and peroxidase. Free hordenine in certain concns. is toxic to microorganisms with the exception of bacteria. If the concn. is not too high it can be utilized as a N source by microorganisms. Hordenine and derivatives are toxic or stimulating in alcoholic fermentation, depending upon the concn. H. R. K.

The hemicellulose of *Alhuc cepa* L. YOSHITAKA HASHITANI *J. Coll. Agr. Hokkaido Imp. Univ.* 14, 57-63(1924).—Galactose, xylose and methylpentose but no mannose, fructose, glucose or arabinose were found in the hydrolytic products of hemicellulose of onion. The hemicellulose of onion consists chiefly of galactose and xylose with a small quantity of methylpentosan. H. R. KRAYBILL.

The relation of the salt concentration of the culture solution to transpiration and root respiration. J. D. NEWTON. *Sci. Agr.* 4, 318-20(1923).—Since the rate of plant-root respiration as related to transpiration is increased when the salt concn. of the culture solution is increased, as the concn. of the culture soln. is increased the plant roots must expend more energy in absorbing a given vol. of soln. H. R. KRAYBILL.

The non-volatile acids of cacao seed pulp and cacao sweatings. FREDERICK HARRY. *J. Soc. Chem. Ind.* 44, 305-6T(1925).—Citric acid is apparently the only non-volatile acid present in either case, its concn. being 0.7% of the fresh pulp. W. B. P.

The growth of duckweeds in mineral nutrient solutions with and without organic extracts. A. SAEGEL. *J. Gen. Physiol.* 7, 317-25(1925).—Inorg. salt solns. (Detmer or Knop soln.) were unfavorable for the growth of *Spirodela polyrrhiza*. In modified Knop soln., dil. to 10 times its vol., *S. polyrrhiza* and *Lemna caldarumana* grew and reproduced for 26 and 21 months, resp. Growth in dil. Knop soln. was considerably stimulated by the addition per l. of the water-sol. material from 0.4 g. autolyzed yeast or the material from 2.5 g. peat sol. in 1%  $NaHCO_3$  soln. The nature of this stimulus is unknown. The necessity of org. accessory foods (auxinones) in the nutrition of green plants is not established. CHAS. H. RICHARDSON.

Further studies on new methods in the physiology and pathology of plants. C. B. LIPMAN AND A. GORDON. *J. Gen. Physiol.* 7, 615-23(1925).—Solns. are introduced into small plants and trees through  $1/8$ - $1/4$  inch holes in the trunk. Into the hole a glass tube is sealed with wax and is connected with a reservoir by means of rubber tubing. The rate of flow of liquid into a tree increases with the height of the reservoir till the top of the tree is reached. It is greater when the soil moisture is low. Pear trees may absorb as much as 63 l. of soln. in 12 hrs. Solns. which have been injected into trees by this method become quickly distributed throughout all portions. After the injection of a dil. soln. of Na arsenate, As was found in leaves and branches within 24 hrs., and the leaves showed injury in 48 hrs. Similar tests were made on pear and apricot trees with dil. KI soln. Methylene blue and methyl green were harmless to trees even in concd. solns; eosin, however, showed marked injury in 3 days after injection. The resistance of individual trees to KI is discussed. Trees injected with dicyanodiamide soln. (0.04%) were injured but recovered; however, solns. of all concns. seemed to retard growth. KCN soln. caused severe injury, with complete recovery except for retarded growth. Mg salts caused decided stimulation, Ca salts were more toxic than Mg or K salts, the latter occupying an intermediate position. These effects may have been due in part to the concns. used. At lower concns. Ca and K salts would probably have stimulating rather than toxic effects. Mg salts are unique in being stimulants at relatively high concns. The period of the year when the injection is made is a large factor in determining the reaction of the tree. Lemon trees affected with chlorosis have been successfully treated by injection with  $FeSO_4$  soln. The permanence of the result must be detd. later. This injection method has practical possibilities in the control of bacteria, fungi and possibly insects which attack plants. CHAS. H. RICHARDSON.

The stimulating action of warm baths. K. BORGESCU. *Biochem. Z.* 153, 313-34 (1924).—Growing plants were studied under the following conditions in 1/10 at

30°; in air satd. with moisture at 30° and 737–57 mm., and at 30° and 20° at 50 mm pressure. The plants observed were *Corylus avellana*, *Forsythia suspensa*, *Syringa vulgaris*, *Sambucus nigra*, *Robinia Pseudacacia*, *Tilia parvifolia*, *Acer platanoides*, *Betula verrucosa*, *Aesculus hippocastanum*, *Alnus glutinosa*, *Quercus pedunculata*, *Ulmus campestris* and *Fraxinus excelsior*. The stimulating effect of warm baths upon resting plants was marked at 30° and 50 mm as well as at 30° and 737 mm pressure. It seems to be due to the high temp. accompanied by a low O concn in the H<sub>2</sub>O. W. D. L.

Carbohydrate utilization by the cell and variations in the nucleus and nucleolus. A. MAIGE. *Cellule* 35, 325–40 (1925).—Sucrose, maltose, lactose, glucose, levulose, galactose, mannose, and glycerol are foodstuffs for the cells of the bean, while mannitol is probably not assimilable. The physiol. utilization, or non-utilization of a carbohydrate is revealed by the changes which take place in nuclear and nucleolar material. In plants which form starch readily the changes can be most readily followed by variations in the nucleolus; where it is formed with difficulty changes in nucleus are most readily detected. The changes which take place occur immediately after the penetration of the foodstuff, thus the cytophysiol. method is quicker and more direct than the ordinary physiol. method of detg. the influence of foodstuffs upon cellular changes. G. H. S.

Non-volatile organic acids of alfalfa. WM. A. TURNER AND A. M. HARTMAN. *J. Am. Chem. Soc.* 47, 2014–7 (1925).—Alfalfa contains citric, malic and malonic acids in notable amts., the citric being present in largest quantity, malic in about 1/2 the quantity of the citric and malonic in about 1/3 that of the citric. Nelson's citric acid trihydrazide (C. A. 18, 313S), m. 145°, is the anhydrous product, that m. 107° contains 1 mol H<sub>2</sub>O. C. J. WEST.

Biochemistry of plant diseases. VI. Biochemistry of *Fusarium lini* Bolley. A. K. ANDERSON. *Minnesota Studies in Plant Science*, No. 5, 237–80 (1924).—To ascertain the chemical basis of certain diseases of plants, the C metabolism of *Fusarium lini* under different growth conditions was studied, the various products were measured quantitatively. The organism was grown on media with initial  $p_H$  values of from 1.84 to 12.04, the range for good growth was  $p_H$  3.5–9.5, the optimum at about  $p_H$  5 in two cases, and  $p_H$  7 in a third case. In most cases there was a change in  $p_H$  toward the acid side during growth. This change is especially noticeable on alk. media; it is due more to CO<sub>2</sub> than to the production of other acids. Some of the decrease in alk. is due to the binding of alkali by the peptone of the medium. After an initial drop in  $p_H$  there is a rise, which may be due to a utilization of org. acids produced in the early stages of growth. The change in reaction is such as to bring the final reaction within the range for good growth. There is a drop in  $p_H$  in alk. peptone medium on standing uninoculated and protected from the CO<sub>2</sub> of the air by soda-lime tubes. The dry matter produced on media with KNO<sub>3</sub>, aspartic acid, urea, asparagine, and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> as the only sources of N decreases in the above order. On the last the decrease is evidently due to the quicker absorption of NH<sub>4</sub> ions than of SO<sub>4</sub> ions, while on KNO<sub>3</sub> the  $p_H$  of the medium increases, evidently because of the more rapid absorption of the NO<sub>3</sub> ions. *Fusarium lini* grows well on glucose, levulose, galactose, mannose, xylose, sucrose, maltose, lactose, sol. starch, and inulin as an only source of carbon. No growth occurs in the closed arm of the fermentation tube. The products of metabolism on glucose are mainly CO<sub>2</sub> and EtOH, with traces of succinic acid and glycerol. More than 90% of the C in the glucose originally present can be accounted for in the unused glucose, CO<sub>2</sub>, EtOH, mycelium, and lead ppt. The ratio of CO<sub>2</sub> to EtOH is nearly that of a typical yeast fermentation. However, the ratio is usually high, because EtOH is utilized by the fungus as a source of C. The initial  $p_H$  of solns. has no effect on the nature or proportion of the products formed. The only effect appears to be in the rate at which fermentation occurs. *Fusarium lini* grows more slowly in xylose than on glucose. CO<sub>2</sub> and EtOH are the main products of metabolism. Eighty % of the original C can be recovered in the EtOH, CO<sub>2</sub>, mycelium, lead ppt., and unused xylose. The proportion of C in EtOH to C in CO<sub>2</sub> on a xylose medium is nearly 1:1 as compared to 2:1 in the case of a glucose medium. *Fusarium lini* grows on EtOH as an only source of C, producing CO<sub>2</sub> as the main by-product. The ratio of C in CO<sub>2</sub> to C in mycelium on EtOH is 1:1, whereas on the sugars it is from 2 to 4:1. The EtOH medium became more strongly acid than any other medium, the final  $p_H$  being 2.57. The fungus will grow on solns. of EtOH up to a concn. of 3.24 g. in 100 cc. The highest concn. so far obtained is 4.33% by vol. of EtOH, and this was on a 10% glucose medium. Succinic acid serves as a C source for this fungus and EtOH and CO<sub>2</sub> are the main products of metabolism. On glucose the percentage of C in the mycelium increases with the age of the mycelium from 40.62% to 52.65%. The percentage of N as a rule decreases slightly. On xylose, there is very

little change in the compn. of the mycelium due to age. On EtOH, the percentage of N in the mycelium is greater than when glucose or xylose is the sole source of C. J. J. WILLAMAN

Constitution and synthesis of natural coloring matters (FURNESS) 10. Alkaline chlorosis of the vine (PRATOLONGO) 15.  $\gamma$ -Galactan contained in the seeds of *Cicer arietinum* (CASTORO) 10.

## E—NUTRITION

PHILIP D. HAWK

Carbohydrate and protein digestion in pigeons and hens and the penetration of digestive enzymes through plant-cell membranes. E. MANGOLD. *Biochem. Z.* 156, 3-14(1925) — There is no amylolytic action in the crop of pigeons but very active starch digestion in the intestinal tract. Penetration of hen's digestive juice into plant cells, such as corn gluten cells, is very slight and digestion awaits rupture of these cells by plasmolysis. F. A. CAJORI

The physiological use, as food, of microorganisms in the stomachs of ruminants. C. SCHWARZ. *Biochem. Z.* 156, 130-7(1925) — An examn. of the N partition of the contents of the first stomach of ruminants during digestion indicates that bacteria furnish an important source of nitrogenous food. F. A. CAJORI

The digestive apparatus of the caterpillar of the clothes moth (*Tinea pellionella*). P. SCHULZ. *Biochem. Z.* 156, 124-9(1925). — The caterpillar nourishes itself largely from keratin from hair. The principle N-contg. end product of keratin metabolism is uric acid. Cystine-S is excreted as  $H_2SO_4$ . Melanin from the hair passes the elementary tract unchanged. F. A. CAJORI

Nitrogen, sulfur and formal nitrogen during feeding of amino acids. R. SEUTTFERT, T. ITO AND T. YOKOIAMA. *Biochem. Z.* 156, 255-61(1925) — The excretion of S and amino-N in the urine of dogs, in negative N balance during a period when the food N was in the form of amino acids, was greater than would be expected from the amt. of N being excreted. Cf. C. A. 19, 1001. F. A. C.

Nutritive value of phosphorus in cattle feeding. J. MARCO. *Intern. Rev. Sci. Practice Agr.* 3, 58-64(1925) — The low P content of cattle feed in Belgian Congo does not cause lamickete—a disease prevalent in the cattle of South Africa on low-P diets caused by the eating of bones of infected carcasses—but does result in osteophagy. This latter condition may be prevented by feeding the animals P. Bone meal was found the most satisfactory means for this. When the diet poor in P is supplemented with P, there is a rapid increase in weight, in milk production, in the strength of calves which they bear, in the quality of the meat, and in the quantity of food consumed and the utilization thereof. The P content of the spring grass was found to be highest while that in the fall had the lowest P content. H. J. DEUEL, JR.

Basal metabolism in obesity. G. BOSCO. *Semana Med.* 2, 573-5(1924); *Physiol. Abstracts* 9, 595 — The low basal metabolism in Fröhlich's syndrome is due to functional or org. changes in the vegetative centers of the hypothalamic region. H. G.

Intarvin in diabetes. MAX KAHN. *Arch. Intern. Med.* 36, 44-50(1925). — Intarvin, fed to diabetics, allays the sense of hunger, makes the patients feel stronger and leads to a gain in wt. Intarvin never produces ketosis nor acidosis nor does it yield glucose. I. GREENWALD

Inulin and artichokes in the treatment of diabetes. H. F. ROOT AND M. L. BAKER. *Arch. Intern. Med.* 36, 126-45(1925) — The use of Jerusalem artichokes proved beneficial to a group of patients who used them for 6 months. They were added to the diet without inducing glucosuria or increasing it, when already present, and when substituted for other carbohydrate food they sometimes rendered the urine sugar-free. During the period of artichoke feeding, the patients were able to increase the other components of their diet and to gain wt. with only a slight increase in the insulin dosage. In all cases, feeding artichokes increased the respiratory quotient. This increase occurred later than after feeding fructose but was more prolonged. The increase in blood sugar after feeding artichokes was definite (0.02 to 0.07% in 3 hrs.) but less than that produced by an equiv. amt. of fructose. Inulin from dahlia tubers did not cause a significant increase in blood-sugar concn. but did lead to a slight increase in the respiratory quotient. The lipoids of the plasma were increased in amt. after feeding artichokes, inulin or fructose, the increase being greatest with the last. I. GREENWALD

Fat-soluble vitamins. XXIII. The induction of growth-promoting and calcifying properties in fats and their unsaponifiable constituents by exposure to light. II.

STEENBOCK AND ARCHIE BLACK. *J. Biol. Chem.* 64, 203-28 (1925).—The effect of irradiation on the antirachitic activity of oils, etc. was studied with the line test, growth and increased Ca content of bone as criteria. A ration of 76 parts yellow corn, 20 wheat gluten, 3  $\text{CaCO}_3$  and 1 NaCl was found more satisfactory for producing rickets than any hitherto reported. Activation was induced by light from the quartz Hg lamp, the open C arc, the Fe arc and by sunlight. The activation rays of the Hg lamp were not able to penetrate the Corning glass filters G-385-DP, G-38-11, G-586-A, window glass nor plate glass but could penetrate thin Pyrex glass and  $\text{H}_2\text{O}$ . Excessive irradiation of both olive oil and cod-liver oil inactivated them. Activated olive oil, kept in a stoppered bottle in the dark for 10 months, retained its activity. The antirachitic potency of irradiated fats lies in their nonsaponifiable constituents. Mineral oil could not be activated nor could old acid oils such as coconut, corn, olea, peanut and cottonseed oils be activated. This was not due to the acid, alone, for the addn. of oleic acid to olive oil did not interfere with the process of activation. The nonsaponifiable constituents of olive oil, added to old coconut oil, could be activated as usual, but the nonsaponifiable fraction of the old oils usually could not be activated. Cholesterol, purified by repeated crystn. and by conversion into the benzoate and acetate, could be activated. Prolonged irradiation of cholesterol, either in crystals or in  $\text{Et}_2\text{O}$  soln., seemed to have no destructive effect on the activity. XXIV. The non-precipitability of the antiphthalmic and antirachitic properties from cod-liver oil by digitonin. R. M. NELSON AND H. STEENBOCK. *Ibid.* 299-312.—"The compds responsible for the antiphthalmic and antirachitic properties of cod-liver oil are non-precipitable by digitonin, A petr.-ether soln. of the unsaponifiable constituents of cod-liver oil standing for 1 1/2 yrs. in the lab. did not lose its antiphthalmic or antirachitic potency. Cholesterol isolated from cod-liver oil was antirachitically inactive, but exposure to ultra-violet light made it active."

I. GREENWALD

The relation of histidine and arginine to creatine and purine metabolism. W. C. ROSE AND K. G. COOK. *J. Biol. Chem.* 64, 325-38 (1925).—On diets in which the N was supplied by casein or by completely hydrolyzed casein, the excretion of total creatinine (creatinine and creatinine), allantoin and uric acid in the urine of rats increased at a rate that was roughly proportional to the increments in body wt. On diets of hydrolyzed casein from which the histidine and arginine had been pptd., the output of allantoin decreased 40 to 50%. The uric acid excretion also decreased, but to a lesser extent. The excretion of total creatinine increased, then decreased somewhat but not to less than the amt. excreted on the control ration. When the diet was adequate except for a deficiency in tryptophan, the animals steadily declined in wt., but the output of allantoin and uric acid remained quite const. The addn. of histidine to the diets contg. the hydrolyzed casein from which histidine and arginine had been pptd. led to increases in the excretion of total creatinine, uric acid and allantoin until the quantities eliminated were of the same order as those in animals upon the casein diets. But the addn. of arginine to the deficient rations failed to affect the excretion of any of these 3 urinary constituents. It may be that the lack of any relation between arginine addn. and total creatinine excretion was due to the fact that none of the diets was completely free from arginine. Arginine and histidine are not interchangeable in metabolism. Histidine is one of the precursors of purines.

I. GREENWALD

A note on the influence of the diet on the synthesis of hippuric acid. W. H. GRIFFITH. *J. Biol. Chem.* 64, 401-7 (1925).—The low figures reported by Abderhalden and Werthelmer (C. A. 19, 1153) for the hippuric acid excretion in rabbits on diets furnishing an alk. urine were due, not to any deficiency in the synthesis of hippuric acid, but to the addn. of insufficient  $\text{HCl}$  to permit of the complete extn. of the hippuric acid. I. G.

A biochemical study of bone growth. I. Changes in the ash, organic matter and water during growth (*Mus norvegicus* albifrons). FREDERICK S. HAMMETT. *J. Biol. Chem.* 64, 409-28 (1925).—White rats were killed and the weight, length,  $\text{H}_2\text{O}$ , org. matter and ash content of the humeri and femurs were detd. In both sexes at all ages, the humerus contains more ash than the femur. At the same age, both bones in the female contain more ash than in the male. The  $\text{H}_2\text{O}$  content decreases progressively with age. A marked drop in growth capacity occurs at 30 days of age, probably as a result of the weaning at 23 to 25 days. There is a second drop, probably due to puberty, at 65 days. In the interval, the rate of growth is characteristic of the sex. Puberty brings these differences to an end.

I. GREENWALD

The calcium content of the body in relation to age, growth and food. H. C. SUMNERMAN AND P. L. MACLEOD. *J. Biol. Chem.* 64, 429-50 (1925).—Rats of different ages were killed and the entire carcass, with the exception of the alimentary tract, was analyzed for Ca. The Ca content of the body increased from about 0.25% at birth to about

0.6% at 15 days, 0.7% at 30 days, 0.75 to 0.85% at 60 days, 0.95 to 1.1% at 90 days and 1.0 to 1.2% in the adult animal. Females which had not raised young showed a higher % of Ca than males of the same age and inheritance that had received the same food, but because, of the greater wt of the males, the total Ca content of the males was greater after 60 days of age. The increase in amt and % of Ca was rapid up to 90 days. It was slower but steady from 90 days to 8 months both in males and in females that had not raised young. In males, there was a slow increase from 8 to 12 months. In females, pregnancy and lactation reduced the Ca content by about 0.1, after which there was an approx. balance between losses due to raising of young and gains in the intervening periods. Animals that had received ample Ca but that had been stunted because of lack of vitamin A or B or too little protein (shortage of cystine) contained more Ca than normal animals of the same wt but less than did normal animals of the same age. The same effect was produced by feeding a satisfactory ration that had been largely did with starch. Animals which receive sufficiently little Ca in their diets lose it from their bodies. Animals on a diet of  $\frac{1}{2}$  milk powder and  $\frac{1}{2}$  wheat contained less Ca than those on a diet of  $\frac{1}{2}$  milk powder and  $\frac{1}{2}$  wheat. Addn of 1% cod-liver oil to the former diet did not raise the % of Ca in the body but the addn. of 1% Ca lactate raised the Ca content to the normal level. I. GREENWALD.

The antiscorbutic vitamin content of milk. A. FRANK, *Klin. Wochschr.* 4, 1204-7 (1925).—Human milk and goat milk have practically no antiscorbutic properties (guinea pig). Cow milk, both raw and as marketed, has considerable antiscorbutic value (Leipzig). The milk used had neither been pasteurized nor treated with preservatives. MILTON HANKE.

Phases of carbohydrate metabolism. E. HELMREICH AND R. WAGNER, *Z. ges. expl. Med.* 45, 490-6 (1925).—A case is reported of a child with an enlarged liver and hepatogenous hypoglycemia who showed disturbance of intermediary metabolism and an anomaly of respiratory metabolism. Oral administration of glucose was followed by an increase of sugar in the blood and glucosuria but the respiratory quotient remained low for 3 hrs. The final rise of respiratory quotient is an indication of the change of sugar to fat but the first stage of normal carbohydrate metabolism, the storing of glycogen, is missing. In contrast to a diabetic there was no accumulation of acetone bodies. The child was extremely insensitive to thyroiodine. H. F. H.

The place of proteins in the diet in the light of the newer knowledge of nutrition. H. H. MITCHELL, *Smithsonian Repts. for 1923*, pp. 223-32 (1925).—Recent work relative to the nutritive value of different types of proteins is summarized, and data are reported for work done at the University of Illinois during the past 5 years. By Thomas' procedure, the bio. value of proteins fed at 5 and 8 (8-10) % levels, resp., to rats, was found to be: veal 97.84, milk 93.85, beef 92.81 (8%), 68 (10%); rice 80.67 (bran); yeast 85.67, oats 79.65, coconut 77.58, corn 72.60, soy bean 73.64; potato 68.67; navy beans (cooked) 29.38; casein 71 (5%); tankage 31 (8-10%); cotton seed 66 (8-10%). The difference in nutritive values between animal and vegetable proteins is not so great as recorded by earlier investigators, but the animal proteins are shown to be distinctly superior. The "net" protein value of a food is taken as the protein content, times the % digestible, times the % available for endogenous metabolism. C. G. KING.

Ultra-violet radiations in conditions of extreme calcium and phosphorus deficiency. HELEN S. MITCHELL AND F. JOHNSON, *Am. J. Physiol.* 72, 143-50 (1925).—Radiations with ultra violet rays proved beneficial to rats on diets deficient in Ca and P; body growth, bone growth and nutritive condition were improved by the treatments. J. F. LYMAN.

Blood regeneration in severe anemia. I. Standard basal-ration bread and experimental methods. G. H. WHIFFLE AND F. S. ROUSCHERT-ROBBINS, *Am. J. Physiol.* 72, 395-407 (1925).—A palatable bread which maintains dogs in health for several months but permits of min. red-cell regeneration is made from wheat flour, potato starch, bran, sugar, cod liver oil, canned tomatoes, compressed yeast, salt mixt. without Fe and water. II. Favorable influence of liver, heart and skeletal muscle in diet. *Ibid.* 408-18.—Beef-liver feeding in severe anemia is associated with maximal blood regeneration; beef heart is distinctly less favorable and skeletal muscle still less so. It is suggested that liver carries the patent pigment substances and that the liver is connected with pigment construction. III. Iron reaction favorable.—Arsenic and germanium dioxide almost inert. *Ibid.* 419-30.—Long continued severe anemia due to hemorrhage may be associated with Fe depletion and in such cases iron treatment (Bland's pills) has a favorable effect.  $\text{GeO}_2$  and As have slight or no influence. IV. Green-vegetable feeding. *Ibid.* 341-5.—In severe exptl. anemia green vegetables are only moderately favorable food factors for the regeneration of hemoglobin. It appears that the normal

dog cannot utilize much if any of the chlorophyll nucleus for hemoglobin construction

J F LYMAN

Effect of calcium carbonate supplement in the diet of hens, on the weight, protein content and calcium content of the white and yolk of their eggs. C D BUCKNER, J. H. MARTIN AND A. M. PEYER. *Am J Physiol* 72, 458-63(1925).—The addn of oyster shell to a poultry ration of corn, wheat and buttermilk increased the total contents of the eggs produced, but had no effect on the Ca and protein concn of the white and yolk.

J F LYMAN

Nutrition with diets rich in protein. V B READER AND J C DRUMMOND. *J Physiol* 59, 472-8(1925).—On food mixts. contg 90% protein rats failed to show normal growth at any stage and attained a const wt of approx 33% of the calcd normal. No abnormalities in body structure were noted except hypertrophy of the kidneys.

J F LYMAN

The effect of iodine on the metabolism of nitrogen and phosphorus in the growing pig. F. C. KELLY. *Proc Physiol Soc, J. Physiol* 59, lxxix(1925).—The addn of 0.25 g. I daily to a low-I ration (cereals) increased the retention of N and P markedly.

J F LYMAN

Light and nutrition. L. HENRI DEJUST. *Bull soc hyg aliment* 13, 199-215 (1925).—Brief review of the function of light in the elaboration of vegetable and animal tissues, and of its importance in the treatment of rickets and spasmophilia. Bibliography of 32 references.

A PAPINEAU-COULRE

A study of the pellagra-preventive action of dried beans, casein, dried milk and brewer's yeast, with a consideration of the essential preventive factors involved. J. GOLDBERGER AND W. F. TANNER. *U S Public Health Ser Pub Health Repts* 40, 54-80(1925).—A liberal supply to protein presumably of good biological quality (casein) does not completely prevent pellagra, but may modify the course of the disease. The prevention and causation of pellagra is brought about by a previously unrecognized factor, called P-P by the authors. It may or may not be effective without the protein factor. Factor P-P is present in brewer's yeast, milk and lean meat, but is of low concn or absent in dry soy beans, dry cow peas, butter, cod-liver oil and canned tomatoes (cf C. A. 18, 1324).

CHAS H RICHARDSON

High-protein ration as a cause of nephritis. N EVANS AND R H RISLEY. *California and Western Med* 23, 437(1925), *J Am Med Assoc.* 84, 1870. —Animals fed on a high-protein ration for prolonged periods showed nephritic changes without exception. Control animals fed ordinary diets showed no kidney changes. Limiting the meat and increasing the fruits and vegetables in the human ration is recommended as an important prophylactic measure in relation to nephritis.

L W RIGGS

Comparative variations of arterial glucemia (effective and proteinic) and the content of glycogen in the liver in the normal pigeon and in the pigeon subjected to a diet deprived of water-soluble B. (MINE) L RANDON AND E LELEZ. *Compt rend.* 180, 1360-8(1925); cf. C. A. 19, 2365. Feeding expts were made on 3 series of pigeons, viz., 27 birds on a natural diet (mixt of grains), 27 on a complete artificial diet, and 36 on an artificial diet deprived of factor B. The birds of the latter series gave figures for blood sugar near those of birds in the other series during the period of about 12 days previous to the exhibition of symptoms. During the period of loss of wt, lowering of temp and paralysis both free and proteinic sugar increased with a further slight increase during the premortal period, the free sugar increasing much more than the proteinic sugar. The glycogen does not disappear from the liver during the course of avitaminosis B when the best artificial diet is given by forced feeding. A diet deprived of factor B prevents neither the storing of glycogen nor the liberation of sugar in the blood, but the organism is deprived of a substance which is directly or indirectly indispensable to the combustion of sugar.

L W RIGGS

Influence of fluorine and of iodine upon the reproductive function of rats and upon the growth of their young. P. MAZE. *Compt rend* 180, 1683-4(1925).—A ration of whole-milk powder maintained rats with unimpaired reproductive faculties, but when fed a ration of skimmed-milk powder the animals were maintained but their reproductive faculties were not assured. Four series of 4 to 6 rats each were fed rations a, b, c, and d, resp., consisting of skimmed-milk powder to which whole-milk powder had been added so that the mixts. contained 0.35 (skimmed-milk powder alone), 1.60, 2.86 and 6.61% of fat, resp. Four other series of rats were fed rations e, f, g, h, resp., which were prepd by adding to the rations a, b, c, and d, 1, 2 or all of the following named salts in the proportions indicated:  $\text{CaHPO}_4$  0.1,  $\text{Na}_2\text{F}_2$  0.01, and  $\text{KI}$  0.005%. All of the animals received 1 cc. of citron juice per rat per day. The results showed that the rats of the first series failed to reproduce. Rats of the second series reproduced about normally.

but with rats fed ration *e* it was necessary to double the proportions of  $\text{Na}_2\text{F}_2$  and KI to insure normal reproduction. The rations *e*, *f* and *g* did not insure normal lactation in the mothers or the growth of the young. This deficiency was made up in ration *f* by the addn. of 8% of olive oil and doubling the  $\text{Na}_2\text{F}_2$  and KI. The  $\text{CaHPO}_4$  was entirely without effect. Expts. are in progress to det. the influence of the fluoride and iodide added separately. L. W. RIGGS

Modifications in the metabolism of meat as determined by cooking. CH. RICHTER, JR. AND R. MONCEAUX. *Compt. rend.* 180, 1688-9 (1925).—Two dogs weighing 6 to 7 kg. were placed in sep. cages and fed lean beef at the rate of 30 g. per kg. for 20 or more days. The beef was fed under the following conditions: raw, half-cooked, boiled 10 min., boiled 60 min., and over-cooked at 115°. The daily urines were collected and analyzed with the usual N partitions. The results proved that the metabolism of raw meat was more nearly complete than that of cooked meat. In hepatic affections there appears an advantage in feeding raw meat, while in renal affections the advantage is with cooked meat. L. W. RIGGS

Avitaminosis C and cholesterolemia. MOURIQUAND, LÉULIER, MICHEL AND ID-RAC. *Compt. rend.* 180, 1699-1701 (1925); cf. *C. A.* 19, 96, 1159.—Acute or chronic avitaminosis C does not appear to exercise any distinct influence upon cholesterolemia. L. W. RIGGS

McCOLLUM, E. V. AND SIMMONDS, NINA: *Newer Knowledge of Nutrition. The use of foods for the preservation of vitality and health.* 3rd ed. entirely rewritten. New York. The Macmillan Co. 675 pp. \$4.25.

## F—PHYSIOLOGY

ANDREW HUNTER

Calcium chemistry of teeth. R. E. LIESEGANG. *Deut. zahnärzt. Wochschr.* 27, 103-4 (1924).—The  $\text{CO}_2$  and other acids produced by intracellular respiration prevent the deposition of Ca carbonate and Ca phosphate in the tissues. The connective tissues in which the Ca salts of bone and teeth are deposited are relatively poor in cells. It is not necessary to postulate sp. Ca fixers. The transparent zone in dental caries is the result of local hypermineralization. B. C. A.

Biochemistry of muscle contraction. W. E. GARNER. *Nature* 115, 532-3 (1925).—If the anisotropy of alternate striae of muscle fiber is due to the presence of oriented mols. of long chains of salts or esters of amino acids, the contraction wave, which is associated with increase of H-ion concn. due to the production of lactic acid from glycogen, may cause liberation of the amino acids, with consequent alteration of the inclination of successive mols. to one another, shortening of the length of the zig-zag composed of a finite no. of mols., and the production of tension along the length of the fiber. B. C. A.

Elimination of amylase by the kidneys. AMBARD AND VAUCHER. *Scalpel* 76, 837-41 (1923); cf. Ambard and Wolf, *C. A.* 18, 3647.—The elimination of amylase is neither by diffusion ( $\text{EtOH}$ ,  $\text{CHCl}_3$ , acetone) nor by secretion (carbamide), but is of a particular type depending on the colloidal nature of the enzyme. The total amt. of enzyme eliminated is unaffected even when the vol. of urine excreted is appreciably increased; it is only slightly affected by variations in the amt. present in the blood. B. C. A.

How is the place of polarization in the physical-chemical theory of electric nerve stimulation to be detected? L. LAFICQUE. *Biochem. Z.* 156, 80-5 (1925).—A review. F. A. C.

Ammonia formation in the nervous system. H. WINTERSTEIN AND E. HIRSCHBERG. *Biochem. Z.* 156, 138-49 (1925).—In confirmation of Tashiro's expts. (*C. A.* 16, 2897),  $\text{NH}_3$  was found to be given off from frog peripheral nerves.  $\text{NH}_3$  production is completely checked by urethan, but when the effect of this narcotic has passed, the rate of  $\text{NH}_3$  production is greater than it was before the narcotic was given. F. A. C.

The influence of homologous alcohols on sugar formation in frog liver. 2. E. J. LESSER. *Biochem. Z.* 156, 161-70 (1925); cf. *C. A.* 18, 1327.—Perfusion of frog liver with 0.7% NaCl soln. contg. ethyl, propyl, and butyl alc. caused an increase in sugar formation by the liver, as measured by the glucose content of the perfusion liquid. The effect of the alcs. on sugar formation was found to be reversible. F. A. CAYORI

The physicochemical condition of stimulation conductance in nerves. I. The dependence of conducting possibility on temperature in the intact living animal. H. ROSENBERG AND T. SUGIMOTO. *Biochem. Z.* 156, 262-8 (1925).—The velocity of stimulation conductance in the motor nerves of living intact frogs (*Rana esculenta*) shows a

considerable temp. coeff. Between  $12.5^{\circ}$  and  $26^{\circ}$ , the temp. coeff. ( $Q_{10}$ ) = 1.56. At room temps.,  $Q_{10}$  = 1.58. Below  $12.5^{\circ}$ ,  $Q_{10}$  rises considerably. F. A. CAJORI

New investigations on the behavior of oxalacetic acid in the animal organism. P. MAYER. *Biochem. Z.* 156, 300-2(1925).—Fresh rabbit muscle was added to a soln. of oxalacetic acid, neutralized with NaOH, and allowed to remain 24 hrs. at  $37^{\circ}$ . At the end of this time a part of the oxalacetic acid had changed to l-malic acid, which was identified by optical methods and analysis of its U salt. F. A. CAJORI

Gasometric and spectroscopic observations of methemoglobin formation. W. KLEIN. *Biochem. Z.* 156, 323-33(1925).—The formation of methemoglobin from hemoglobin and oxyhemoglobin and the influence of various reagents on its formation was followed by gasometric detn. of O in blood and observation of the characteristic absorption bands of the blood pigments. The change of hemoglobin to methemoglobin involves a change of  $Fe^{++}$  to  $Fe^{+++}$  in the hemoglobin mol. and the liberation of acid  $FeSO_4$ ,  $FeSO_4(NH_4)_2SO_4$ ,  $H_2SO_4$ , citric, tartaric and succinic acids change part of the hemoglobin to methemoglobin. Succinic acid is recommended as a reagent for direct detn. of  $CO_2$  in blood. F. A. CAJORI

The source of energy in muscle work. G. LUSK. *Biochem. Z.* 156, 334-42(1925).—A review of the exptl. work on the chem. changes involved in muscular work. The Hill-Myerhoff theory of the recovery process does not explain all the facts. There are data showing that fat is oxidized directly and does not first change to lactic acid. If the latter occurred, the theory of ketogenic-antiketogenic balance would have to be discarded. F. A. CAJORI

The action of fluorine on the work capacity and the lactacidogen metabolism of frog muscle. G. EMBDEN AND H. HENTSCHEL. *Biochem. Z.* 156, 343-52(1925).—The increase of  $H_2PO_4$  in frog gastrocnemius muscle during repeated contraction is much greater when the muscle has been treated with NaF than when it has not. F ion causes greater formation of lactacidogen. F. A. C.

Observations of the blood sugar of goats. K. SCHUECKER. *Biochem. Z.* 156, 353-64(1925).—The blood sugar of normal goats is lower than that of other animals (49-60 mg. per 100 cc.). There is very little diurnal variation in the sugar content. There was rise in the blood sugar of these animals following exercise (running) and after small doses of adrenaline. Marked hypoglycemia (17-29 mg. per 100 cc.) followed insulin injection. F. A. CAJORI

Nitrogen distribution in the oxyproteic acid fraction of urine. S. EDLBACHER. *Z. physiol. Chem.* 144, 278-9(1925).—Polemical against Brings (C. A. 19, 1448). A. W. DOX

The significance of ions for the muscle function. VIII. The action of various alkali salts on the fermentative degradation of glycogen in frog-muscle pulp. JULIUS WEBER. *Z. physiol. Chem.* 145, 101-29(1925); cf. C. A. 19, 1590.—The fermentative cleavage of the glycogen present in frog muscle can be influenced in large measure by ions. A reversible process capable of being influenced by the play and counter-play of ions, such as occurs in lactacidogen metabolism, could not be observed with surviving frog-muscle pulp because of the lack of hexose in sufficient amt. for such syntheses; hence a glycogen synthesis could not be established. However, it was shown that individual ions inhibit glycogen cleavage, others accelerate it, and still others act in either direction according to their concn. By arranging the anions in the order of their activity, it was found that they follow the Hofmeister series, i. e.,  $SCN$ , I, Br and  $NO_3$  in decreasing order retard glycogen cleavage. Cl may act in either direction. Acetate, sulfate and tartrate have an accelerating effect, also citrate to a smaller extent, while oxalate and fluoride retard cleavage. The auxoclastic action of Cl acquires significance from the fact that Cl ions are an important factor in muscular activity. The anions of phosphoric, lactic and succinic acids promote glycogen cleavage. The auxoclastic effect of lactic acid is significant in view of the fact that the lactic acid ion promotes the synthesis of lactacidogen. Under suitable conditions phosphate and lactate have an additive effect in promoting the cleavage of glycogen. A. W. DOX

A new cerebroside from the brain. E. KLENK. *Z. physiol. Chem.* 145, 244-60(1925).—From both beef and human brain a new cerebroside was isolated for which the name *nervon* is proposed. This cerebroside is found in the  $Et_2O$  or petroleum-ether fraction along with the unsatd. phosphatides and is very similar in its properties to kersin. The cleavage products are galactose, sphingosin and a new unsatd. fatty acid  $C_{17}H_{32}O_2$ , m.  $41^{\circ}$ . On the basis of m. p. and other properties this acid fits into the series of natural fatty acids  $C_nH_{2n-18}O_2$ . Elementary analysis of nervon gives the formula  $C_{47}H_{81}O_{12}N$ , which is in agreement with the sum of the 3 cleavage products— $2H_2O$ . A. W. DOX

Organic bases from urine. JULIE HEFTER *Z. physiol Chem* 145, 290-4(1925) — In working up 40 l of urine by the  $\text{HgSO}_4$  method, which pptd. carnosine from very dil. solns., 0.1 g. histidine was obtained but no carnosine. A. W. DOX

Character of respiration, its explanation. OTTO WARBURG. *Pharm. Monatshefte* 6, 105-6(1925) — It is shown that without Fe life would be impossible. Its fate in the animal economy is explained. W. O. EMERY

The colostrum of the cow. HEINZ ENGEL AND HANNA SCHLAG *Milchwirtschaft. Forsch.* 2, 1-15(1924) — A complete analysis is given of the colostrum of 3 cows. At the beginning of lactation the sp. gr., acidity, NaCl, N and total solids are high while the lactose and refraction of  $\text{CaCl}_2$  serum are low. The % fat,  $\text{P}_2\text{O}_5$ , CaO, MgO and NaCl vary somewhat during the colostrum period. The absolute ash content is somewhat higher than in natural milk but the ash content of the milk solids is somewhat lower. O. L. EVENSON

Tissue respiration and biological oxidation. HANNS LÖHR *Klin. Wochschr.* 3, 1038-40(1924) — A bibliographical review. MILTON HANKE

Contraction of skeletal muscle by ammonia. OTTO RIESSER AND NAGAYOSHI HEIANZAN *Klin. Wochschr.* 3, 1060-2(1924) — See *C. A.* 19, 1591. MILTON HANKE

The effect of neutral salts on the excretion of acids into the urine. P. GYÖRGY *Klin. Wochschr.* 3, 1225-6(1924) — The daily ingestion of 5 g. NaCl or KCl leads to an increased excretion of acid into the urine unless the ingested salt produces fever. Salt fever is associated with a decreased excretion of acid. *Cf. C. A.* 19, 1596. M. H.

Experimental transmineralization of the blood. M. RICHTER-QUITZNER *Z. ges. exper. Med.* 45, 479-83(1925) — In rabbits oral and intravenous administration of  $\text{CaCl}_2$  increases the Ca content and diminishes the Na content of the blood, the K content showing no regular change. No transmineralization could be made out in any organ. NaCl and  $\text{NaHCO}_3$  increase the Na and diminish the Ca and K contents.  $\text{MgCl}_2$  leads to an increase of Mg and a decrease of Ca in the blood plasma. Ordinarily all the Na, K, Cl and 80-90% of the Ca salts pass the ultrafilter of Glomerula but after the administration of  $\text{MgCl}_2$  89% of the total Ca becomes ultrafilterable, indicating that it is possible to alter experimentally the phys. condition of the Ca of the blood. HARRIET F. HOLMES

The measurement of the diameters of erythrocytes. II. The effect of drying on the diameter of the red cells in man. ERIC PONDER AND W. G. MILLAR *Quart. J. Exper. Physiol.* 14, 319-26(1925) — The frequency curve for dry cells is deduced from a photographic study of 700 corpuscles. Measurements were made in plasma and in the dried condition. Close agreement was obtained between these findings and the calcd. values. FRANCES KRASNOW

Respiratory changes during and after a period of anoxemia. E. C. SCHNEIDER, DOROTHY TAUBSDALL AND R. W. CLARKE *Am. J. Physiol.* 71, 714-28(1925) — Respiratory changes and  $\text{CO}_2$  elimination were detd. in human beings during anoxemia produced by low air pressure, and its subsequent relief. The results more nearly conform to Gesell's theory (*C. A.* 17, 3531) of the control of respiration than to any other. J. F. LYMAN

Influence of glands with internal secretions on the respiratory exchange. VIII. The effect of feeding emulsions of the interrenal gland to rabbits. DAVID MARINE, E. J. BAUMANN AND ANNA CIPKA *Am. J. Physiol.* 72, 248-52(1925) — The administration of glycerol emulsions of the fresh ox interrenal gland (suprarenal cortex) to rabbits usually caused a distinct fall in heat production, beginning 5 to 7 days after feeding of the gland commenced and persisting usually 4 to 8 days after feeding stopped. J. F. LYMAN

The maximum of human power and its fuel. From observations on the Yale University crew, winner of the Olympic championship, Paris, 1924. Y. HENDERSON AND H. W. HAGGARD. *Am. J. Physiol.* 72, 264-82(1925) — The max. power of a trained oarsman was measured on rowing machines, or by a dynamometer while towing a loaded racing shell behind a launch, at about 0.57 horse power. Measurements of  $\text{O}_2$  consumption and  $\text{CO}_2$  production while rowing showed that either carbohydrates or fats are available for work but that the work can be done more advantageously on carbohydrate fuel. An oarsman may exert a power exceeding by 30 to 50% that afforded by the  $\text{O}_2$  simultaneously absorbed, and he may incur an  $\text{O}_2$  deficit of 4 to 8 l. J. F. L.

The presence of secretin in the intestinal juice. G. W. VOLNBORTH *Am. J. Physiol.* 72, 331-6(1925) — Intestinal juice collected from Thury-Vella fistulas always contained secretin in its sediment. Gastric juice contained a small amt. of secretin, other digestive fluids did not. J. F. LYMAN

## G—PATHOLOGY

H GIDEON WELLS

A study of ragweed pollen extracts for use in the treatment of ragweed pollen hypersensitiveness. CHARLES ARMSTRONG AND W. T. HARRISON. U S Pub. Health Service, *Pub. Health Repts* 39, 2422-8(1924), cf *C A* 18, 3420.—The complement fixation offers a sensitive criterion of the keeping qualities of an ext. A glycerol ext. of mature ragweed pollen was found sp., stable, potent and bacteria resisting, and kept for a long period without deterioration. No antibodies were demonstrated in the sera of patients either before or after prophylactic treatment. Short and giant ragweed pollen exts. tested with their respective antisera gave cross fixation but could not be distinguished from each other by the relative strength of the reactions. H. J. DEUEL, JR.

Analysis of hypoglucemic conditions and the identity of "glucoprivative intoxication" with the "hypoglucemic reaction." F. FISCHLER AND F. OTTENSOOSER. *Z. physiol. Chem.* 144, 1-50(1925).—Under the influence of lack of blood sugar, toxic symptoms occur which may result in death a phenomenon which was recognized by F. in 1913 and for which the term glucoprivative intoxication was proposed. This glucoprivative intoxication corresponds to the hypoglucemic reaction described 6 years later by the discoverers of insulin, but has not been mentioned by them. Further expts. with normal rabbits confirm the identity of the 2 phenomena. Hypoglucemias produced by starvation, by starvation-phlorhizin and by insulin are distinguished as chronic, sub chronic and acute hypoglucemias. Certain differences in their clinical picture are thus explained. In glucoprivative intoxication the advanced toxic effect can be cured by the proper administration of glucose. Loss in wt., fall in temp. and urobilinuria are characteristics of sub chronic hypoglucemia. New evidence is adduced for the possibility of a non-enterogenous urobilinuria. A. W. DOX.

Investigation of a salivary stone. WILHELM PETROU. *Z. physiol. Chem.* 144, 97-100(1925).—A salivary stone weighing 6.09 g. gave the following analysis:  $H_2O$  47.8,  $Et_2O$ -sol. 0.49,  $H_2O$ -sol. 2.18, insol. org. matter 11.80,  $CaO$  43.42,  $MgO$  0.49,  $P_2O_5$  36.20,  $CO_2$  0.08%. Traces of Cl, Na, K and Fe were present, but tests for F,  $SO_4$ ,  $SiO_2$  and SCN were negative. 0.0114% uric acid was found but no ovalate. The presence of diastase was demonstrated. A. W. DOX.

Glucuronic acid, F. VAN DOOREN AND P. DESTREE. *Bruks. med.* 4, 1202-6(1924); *Physiol. Abstracts* 9, 586.—Human urine always contains glucuronic acid. Normal urine treated by Grimbart-Berneck's or by Roger's method shows a red or violet color of the ether after remaining 40 min. in a boiling water bath. Urine from patients affected with hepatic diseases, treated in the same way, shows no color. H. G.

Changes in the suprarenals in experimental scurvy, including some statements on the condition of the bones. T. IWABUCHI. *Beitr. path. Anat.* 70, 440-58(1922); *Physiol. Abstracts* 8, 481.—In exptl. scurvy here are characteristic changes in the suprarenals, consisting of diminution of the lipid of the cortex and loss of the doubly refracting substance of the medulla. The suprarenals of underfed guinea pigs show, on the other hand, increase of the cortical lipid with loss of the doubly refracting material. H. G.

Experimental studies in diabetes. V. Acidosis. 3. Acidosis in dogs without glucosuria. F. M. ALLEN. *J. Metabolic Research* 4, 189-97(1923), cf *C. A.* 18, 2750.—Von Noorden and Mohr state that dogs kept on carbohydrate diet and then subjected to fasting develop acidosis as do human beings. A. attempted to verify this, but obtained negative results. Extirpation of most ( $1/10$  to  $1/12$ ) of the pancreas failed to produce diabetes. Obese dogs showed no special disposition toward acidosis. Preparatory deprivation of sugar by phlorhizin, and adrenaline injections during fasting were tried, but acetonuria was "absent or trivial" throughout. Severely diabetic dogs showed a slightly increased liability to ketosis on high-fat diets or fasting. Two pregnant collies displayed a particular susceptibility to acidosis, but it is not certain whether this was due to the breed or to individual idiosyncrasy. 4. Acidosis in puppies. *Ibid.* 199-222; cf. Neubauer, *Abderhaldens Handbuch d. biochem. Arbeitsmethoden* 1912, V., ii, 1216-17.—These expts. owe their inception to the prevalent belief that children are more subject than adults to acidosis. Pups 1 to 4 months old did prove decidedly more susceptible than mature dogs. The acidosis is produced by about 2 days' fasting; it is aggravated by fat feeding, and prevented by small quantities of carbohydrate or protein. Above the age of 9 months, the behavior begins to resemble that of an adult, but expts. to det. exact age limits were inconclusive, owing to different degrees of acidosis in different animals (individual idiosyncrasy or unknown factors). Pups of the op-

timum age are, however, subject to early death. This cannot be due to starvation or ketone or acid poisoning. It is concluded that the fatal element in ketosis is some metabolic disturbance deeper than that assumed by the traditional chem. theories. Inasmuch as normal pups are highly susceptible to acidosis, it was anticipated that diabetic ones would be well-suited to a study of diabetic coma. This was found not to be the case, both totally and partially depancreatized pups are failures for purposes of acidosis study. They are prone to go into cachexia, and die before an appreciable acidosis has developed. Facilities were lacking for solving a number of problems to the author's satisfaction. Six pages of discussion of the whole problem of exptl. and clinical diabetes are appended, stating questions to be settled before generalizations can be made.

5. Acidosis in phlorhizinized dogs. F. M. ALLEN AND MARY B. WISHART. *Ibid* 223-34.—An attempt was made to learn something of the character and conditions of phlorhizin ketosis, but "only the surface of the problem has been touched." Non-diabetic and diabetic dogs were used. (1) Non-diabetic dogs. Fasting produces a more rapidly dangerous acidosis in phlorhizinized dogs than protein-fat diet. Several early and unexpected deaths of the dogs under observation indicate that the ketones do not themselves cause death. Given sufficiently early, carbohydrate will always revive phlorhizinized dogs, but it is definitely established that some injurious metabolic disturbance takes place which cannot be reversed, if the carbohydrate treatment is too long deferred. The nature of this disturbance is unknown, for there is as yet no chemical test by which it can be recognized. Neither ketonuria nor ketonemia shows any parallelism with the curve of plasma bicarbonate. The fatal intoxication was observed in individuals whose ketonemia was never very high, or the plasma bicarbonate very low.

(2) Diabetic dogs. The animals were rendered potentially diabetic by removal of  $\frac{1}{10}$  to  $\frac{1}{15}$  of the pancreas. Strength and spirits are much better retained with phlorhizin than with true diabetes. The necessity of distinguishing between acidosis and "phlorhizin poisoning" due to hypoglycemia is stressed. Carbohydrate or protein added to the fat in the diet of a diabetic dog does not prevent acidosis and coma, but does prevent dangerous acidosis in dogs with phlorhizin glucosuria. More evidence is obtained that "lack of insulin is far more serious than lack of carbohydrate." (Cf. C. A. 18, 2760) "There is no impairment of the diabetic tolerance with phlorhizin, but rather the reverse." The pancreatic island function is not injured by phlorhizin, but on the contrary is spared, on account of the loss of more sugar in the urine than is contained in the carbohydrate of the diet. The above observations require explanation before the setting up of the theory that ketosis is detd. solely by the ratio between carbohydrate and fat combustion, is justified. The fatal disorder attending diabetic coma is not a mere intoxication with ketones or a poisoning with acid, but an unknown metabolic derangement of which these chemical signs are only a superficial and variable expression."

6. Ketosis in Eck-fistula dogs. F. M. ALLEN AND ALBERT H. EBERLING. *Ibid* 423-30.—The object of these expts. was to obtain evidence for or against the predominant formation of ketones in the liver during acidosis (cf. Fischer and Kossow, C. A. 8, 524). The Eck fistula was used to diminish the amt. of venous blood reaching the liver, and the "reversed" Eck fistula to increase it. "Although the degree of permanent increase of blood flow through the liver with the reversed Eck fistula is doubtful," a definite and invariable tendency to more pronounced ketosis in dogs with the "reversed" fistula than in the Eck dogs would indicate strongly that the liver does have a ketone-forming function. Owing to individual idiosyncrasies, no rigid comparison with normal controls was feasible, but ketosis of the Eck dogs was compared in a general way with that of the normal dogs. After recovery from the operation, ketosis was produced as usual by fasting followed by phlorhizin. Accidents made necessary the rejection of the data on most of the animals, but in every case in which the exptl. program was completed, no obvious alteration in the degree of ketosis was caused by the Eck fistula. The expts. thus fail to support the statements of F. and K., which seem contrary to the best modern conceptions of metabolism.

T. B. GRAVE

Physical and physico-chemical changes in blood in experimental nephritis. J. MOSONYI. *Z. klin. Med.* 98, 500-5(1924).—Dogs were used as exptl. animals. Poisoning with cantharidin had no influence on the elimination of N, but produced first a rise in the f. p. of the blood to  $-0.512^{\circ}$ , followed by a gradual return to normal. Poisoning with U caused marked N retention, a rise in the f. p. of the blood to  $-0.53^{\circ}$ , followed by a decrease to  $-0.638^{\circ}$ , and then a return to normal after repeated small increases. Poisoning by  $HgCl_2$  produced an increase in the N content of the blood, followed, after 7 days, by a decrease to a value markedly below normal; the low value persisted until the termination of the illness.

B. C. A.

The antigenic properties of lysozyme-dissolved vaccines. V. D. ALLISON. *Brit.*

*J. Exptl. Path.* 6, 99-108(1925); cf *C. A.* 18, 2917.—When organisms dissolved by a lysozyme-contg. substance are injected into animals, there is a well marked increase in bactericidal power, with formation of sp. complement-fixing substances. There is also a slight rise in the opsonic power but no increase in the bacteriolytic, pptg. or agglutinating powers.

HARRIET F. HOLMES

Non-specific stimulation of antibodies: the effect of manganese on agglutinins. R. S. HORGAN. *Brit. J. Exptl. Path.* 6, 108-11(1925).—Intravenous injection of  $MnCl_2$  in rabbits appeared to stimulate the agglutinin production in 3 only out of 6 animals. The Mn had apparently no effect in preventing the normal fall from the primary peak. Colloidal Mn gave negative results. There is possibly some connection between the potentiality of an animal to produce antibodies and the power of response to the non-specific stimulation of Mn.

HARRIET F. HOLMES

The antigenic properties of precipitates produced by the interaction of diphtheria toxin and antitoxin. P. HARTLEY. *Brit. J. Exptl. Path.* 6, 112-22(1925).—The ppts. produced from mixts. of diphtheria toxin and antitoxin are insol. in normal saline. The washed ppt. contains less than 1% of the N compds. of the original mixt. Such washed ppts. are antigenic, the antigenic value varying with the nature of the original toxin-antitoxin mixt. If antitoxin is in very large excess the antigenic value of the resulting ppt. is low. The most active prepn. was obtained from a mixt. which was slightly toxic for guinea pigs.

HARRIET F. HOLMES

The etiology of milk fever in cattle. W. L. LITTLE AND N. C. WRIGHT. *Brit. J. Exptl. Path.* 6, 129-34(1925).—Determinations of the Ca content of the blood-plasma of cows suffering from milk fever show that considerable diminutions (in mild cases 20-30%, in severe cases up to 60%) accompany the onset of this disease. No significant increase in the "total acetone bodies" of the blood or urine was noted in these cases.

HARRIET F. HOLMES

Studies on edema. I. The electrolyte concentration in the body fluids in nephritis with edema. J. MARRACK. *Brit. J. Exptl. Path.* 6, 135-8(1925).—The concn. of electrolytes in the body fluids in nephritis with edema is low, and may be definitely below the normal range. The theory commonly taught is that the kidney fails to excrete salt, and that in consequence  $H_2O$  is retained to keep down the osmotic pressure of the body fluids. The condition found appears more like a failure to excrete  $H_2O$  with a compensatory retention of salt to keep up the concn.

HARRIET F. HOLMES

The pathology of respiratory metabolism. II. The action of parenterally introduced protein on basal metabolism, its relation to externally introduced (specific dynamic action of) protein and the relations of both reactions to basal metabolism. H. POLITZER AND E. STOLZ. *Wiener Arch. inn. Med.* 10, 137-64(1925).—The specific dynamic reaction of parenterally introduced protein is comparable to that of externally introduced protein. The max. of the parenteral reaction being reached in 8 hrs., and of the external in 4 hrs. An intramuscular injection of 2 cc. of a 5% soln. of casein increased O consumption about as much as the ingestion of 250 g. of meat.

H. P. H.

Experimental study of the detrimental effects of proteins in diabetes mellitus. L. ERNST AND K. TÓTH. *Wiener Arch. inn. Med.* 10, 339-50(1925).—After verification of the observation of Shaffer (*C. A.* 15, 3307) that the oxidation of acetoacetic acid by  $H_2O_2$  is accelerated in alk. soln. by dextrose, the effect on the reaction of various proteins, protein split-products and other substances was tried. The action of dextrose was inhibited by glycine, aspartic acid, glutamic acid, tyrosine, histidine and uric acid. Without inhibiting effect were alanine, valine, leucine, creatine, nucleic acid, glucosamine, acetic acid, oxalic acid, urea and glycerol. Lactic and tartaric acid had only a slight inhibiting action, and casein was only effective on standing for some time in a warm alkaline solution. It is probable that the inhibiting substances form combinations with the dextrose and thus hinder the favoring of the oxidation by dextrose.

HARRIET F. HOLMES

Study of the extracts used in the Wassermann and Sachs-Georgi reaction with particular reference to their cholesterol content. M. FRANK. *Wiener Arch. inn. Med.* 10, 357-68(1925).—In both the Wassermann and Sachs-Georgi reactions, the actual value of cholesterol necessary in the alc. ext. of the antigen varies between narrow limits. The titer value of the ext. can be computed by detg. its cholesterol content. In the Wassermann reaction diln. with NaCl has no effect, indicating that it is not the percent but the abs. value of the cholesterol content of the ext. that is of importance.

HARRIET F. HOLMES

The reaction of the blood vessels in experimental tuberculosis. A. M. PREOBRAZHENSKI. *Z. ges. exptl. Med.* 45, 452-9(1925).—With the ears of rabbits as test objects, tuberculin shows strong vasodilator power in normal animals. In tuberculous

animals at an early stage of infection, there is an increased sensibility to tuberculin and in cachectic toxic tuberculosis a reduced sensibility. The action of the tuberculin is proportional to its concn., and is analogous to the action of the bouillon with which it is prep'd and seems dependent on the peptone content. Adrenaline causes the same vasoconstriction in the ear vessels of normal as of tuberculous animals and does not increase the effect of tuberculin. Caffeine, however, in toxic tuberculosis, does not produce its characteristic vasodilator effect

HARRIET F. HOLMES

The arterial blood pressure in the tuberculin reaction. L. CALIFENO. *Z. ges. exp'l Med.* 45, 484-9(1925).—The intravenous injection of 5 cc. tuberculin in tuberculous rabbits has no specific action on the blood pressure, the slight rise being due to unspecific components of the tuberculin. In this respect there is a difference between the action of tuberculin and the anaphylactic reaction, for in anaphylaxis the injection of the antigen in a sensitized animal leads to a fall of blood pressure. Sterile conc'd. glycerol bouillon in a 5-cc dose causes a marked fall of blood pressure. This is probably connected with its peptone content, while in tuberculin the peptone has been changed through the action of the tubercle bacilli into hydrolytic split products with more simple mols. which do not have the same effect on blood pressure as peptone. H. F. H.

Pathogenesis of bronchial asthma. II. Urobilinogenuria and the hemoclastic crisis. KARL HAJÓS. *Z. ges. exp'l Med.* 45, 503-8(1925).—In bronchial asthma there is a transitory and periodic disturbance of liver function often accompanied by urobilinogenuria and a hemoclastic crisis shown by alteration in colloid stability in the blood

HARRIET F. HOLMES

Asthma. Its causation and treatment. JAMES ADAM. *Am. Med.* 31, 310-28(1925).—Discussion.

Bronchial asthma. BURTON HASELTINE. *Am. Med.* 31, 328-37(1925).—Discussion

FRANCES KRASNOW

Asthma from an endocrine standpoint. MAXIMILIAN KERN. *Am. Med.* 31, 341-4(1925).—Discussion showing that the endocrine factor may be responsible for conditions which have an intimate relation to asthmatic attacks.

F. KRASNOW

Treatment and prognosis of bronchial asthma. A. W. LA FORGE. *Am. Med.* 31, 345-59(1925).—A review, including a discussion of the metabolic disturbances causing the state of toxicosis

FRANCES KRASNOW

Recent studies in bronchial asthma in infants and children. R. H. KUHN. *Am. Med.* 31, 360-4(1925).—Case reports and discussion

FRANCES KRASNOW

The urine in toxemia. CLIFFORD MITCHELL. *Am. Med.* 31, 371-3(1925).—Case reports and discussion

FRANCES KRASNOW

The significance of lecithin hemolysis for the theory of black water fever. A. KESSLER. *Arch. Schiffs-Tropen Hyg.* 29, 153-62(1925).—Lecithin itself enhances the hemolytic effect of quinine. However, sera with high lipin content do not increase quinine hemolysis *in vitro*

FRANCES KRASNOW

Experiments on the onset of immunity after inoculation with Haffkine's antiplague vaccine. The absence of a "negative phase." W. D. H. STEVENSON AND R. J. KAPADIA. *Indian J. Med. Research* 12, 553-9(1925).—There is no period of increased susceptibility of rats to plague after the administration of antiplague vaccine. The production of immunity among rats commences within a few hrs. of inoculation and increases for the first 2 or 3 days.

FRANCES KRASNOW

A report on the prophylactic inoculation of Indian troops in the Baluchistan district against pneumonia. R. H. MALONE. *Indian J. Med. Research* 12, 565-70(1925).—Pneumococcus vaccine afforded no protection against pneumonia caused by all types of pneumococcus

FRANCES KRASNOW

Estimation of blood sugar in normal rabbits inoculated subdurally with rabies fixed virus. J. W. CORNWALL. *Indian J. Med. Research* 12, 581-2(1925).—There is a slight rise followed by a fall, in blood sugar 24 hrs. after the intracranial injection.

FRANCES KRASNOW

Complement fixation and globulin content in the blood of the lepers. I. The Wassermann reaction given by the lepers' sera. W. D. H. STEVENSON. *Indian J. Med. Research* 12, 583-94(1925).—The incidence of a strongly positive reaction is greater for the tubercular cases than for the anesthetic. II. The globulin content of lepers' sera. *Ibid* 594-600.—High globulin content does not always parallel a strongly positive Wassermann reaction. A drop in the globulin content may be the first indication of improvement under treatment.

FRANCES KRASNOW

Observations of glucosuria and blood sugar content in kala-azar. E. D. W. GREIG AND S. KUNDU. *Indian J. Med. Research* 12, 695-700(1925).—Report of a case

of severe glucosuria complicating kala-azar which on treatment with urea stibamine and insulin showed complete recovery

FRANCES KRASNOW

The "blood meal" of *Phlebotomus argentipes* identified by precipitin antisera. R. B. LLOYD, L. E. NAPIER and R. O. SMITH *Indian J. Med. Research* 12, 811-8 (1925).—"Identification of the blood contained in *Phlebotomus argentipes* by sp. antisera gave striking confirmation of an idea deduced from field observations." The insect will feed on cows in preference to man. Since *Phlebotomus argentipes* is the possible transmitter of kala-azar, a line of prophylaxis against this disease is suggested.

FRANCES KRASNOW

Researches on human serum with special emphasis on serum from epileptics. O. B. MEYER. *Z. Biol.* 82, 417-34 (1925).—During the interval period, the serum from epileptics does not affect the arteries differently from the serum of healthy individuals. A strong contraction of the vessel was obtained immediately after an attack. While the artery muscle in contact with normal serum subsides with spontaneous rhythm, that in contact with epileptic serum either does not react or does so only to a small degree. This effect has not been obtained for sera from other diseases. F. K.

The Kodama reaction for syphilis. E. JACOBITZ and ENGERING *Centr. Bakt. Parasitenk., I Abt.* 89, 116-20 (1922).—The Kodama reaction consists essentially of placing a layer of 0.5-1.0 cc. of specially prep'd (ether 2 days, evap'd., alc. ext'd 2 wks.) ext. of guinea-pig heart or liver, over 0.1 cc. of the suspected serum in Uhlenhuth tubes. Formation of a ring at room temp. is a positive reaction. This reaction when compared with the Wassermann and Sachs-Georgi reactions gave a good agreement in + + + +, + + + or negative sera. The inability of the test to reveal intermediate degrees makes it less efficient than the Wassermann or Sachs-Georgi tests. JULIAN H. LEWIS

Preservation of precipitating antiserum. H. BERKER *Centr. Bakt. Parasitenk., I Abt.* 89, 210-3 (1922).—As a substitute for the more costly filtration through Berkefeld filters, B. recommends the simpler and cheaper method of adding a strip of Cu foil to the antisera for 10-14 days for its preservation. He obtained good results where bacterial spores or molds were not involved. The addn. of "Yatren" was not recommended.

JULIAN H. LEWIS

The practicability of using dry complement in the Wassermann reaction. K. E. F. SCHMUTZ. *Centr. Bakt. Parasitenk., I Abt. Orig.* 94, 177-85 (1925).—It is practicable.

JOHN T. MYERS

Mechanism of acidosis. LEON BLUM and MAURICE DELAVILLE. *Compt. rend.* 180, 1294-6 (1925).—Acidoses are classified as keto acidosis, such as occurs during carbohydrate fasting and in diabetes, lacto-acidosis after severe and prolonged muscular exertion; chloro-acidosis by an excess of HCl observed in nephritis and after the administration of large amts. of  $\text{CaCl}_2$  or  $\text{NH}_4\text{Cl}$ , protein-acidosis in which the proteins monopolize the bases, as observed in certain cases of heart disease with edema. Acidosis by hypoalkalosis is not rare, and acidosis by hyperacidity and hypoalkalinity is encountered in nephritis and in extreme phases of diabetes. L. W. RIGGS

Plurality of toxins of *Bacillus coli* and the experimental bases of anticolibacillic serotherapy. H. VINCENT. *Compt. rend.* 180, 1624-6 (1925).—Colibacillic infection may produce an exotoxin which is a neurotrope, or an endotoxin which is an enterotrope. These may be sepd. by taking advantage of the greater thermostability of the latter. Immunization to one of these toxins does not protect the subject against the other toxin. L. W. RIGGS

High blood sugar with the absence of sugar in the urine in diabetes treated with insulin. R. H. MAJOR and R. C. DAVIS. *J. Am. Med. Assoc.* 84, 1798 (1925).—In 28 detns. of blood sugar in 7 insulin-treated diabetics under 38 years of age and in one patient aged 72, the sugar ranged from 196 to 425 mg. per 100 cc., with 17 of the detns. above 300 mg. Sugar was absent from the urine in every case. It is believed that the estn. of urinary sugar is a safer guide to therapy than the estn. of blood sugar. L. W. RIGGS

Ivy poisoning. Preventive treatment with especial reference to the element of individual susceptibility. G. L. KRAUSE and F. D. WEIDMAN. *J. Am. Med. Assoc.* 84, 1996-9 (1925).—Tests were made on 20 human volunteers of which 16 were susceptible to the poison and 4 were proved to be immune even when the poison ext. of *Rhus toxicodendron* was applied to the abraded skin. It was confirmed that: The discharge from the lesion does not disseminate the disease. The virus itself must come in contact with the part. Susceptible individuals may contract ivy poisoning at any time of the year, provided the juice of the plant comes in contact with the skin. As new findings it is reported that. Repeated attacks tend to shorten all the stages of subsequent attacks. Local immunity is not developed by repeated attacks. Absolute

(and probably permanent) immunity occurs. Among the volunteers  $\frac{1}{2}$  of the men who believed themselves immune were not immune. In 45% of the susceptibles some defect in the epidermis was necessary, such as scratches, before a dermatitis would develop. The commoner lab. animals appear immune to this virus. The antigen treatment of Strickler does not protect against ivy poisoning. L. W. RIGGS

The causal mechanism of diabetes mellitus. A. A. EPSTEIN. *J. Am. Med. Assoc.* 85, 29-30(1925).—Changes in the permeability of the capillary vessels can result in the passage of trypsin into the blood stream, and its ultimate entry the liver via the portal circulation. The first effect of the mobilization of trypsin is a glycogenolysis with a consequent hyperglucemia and glucosuria; the second is the neutralization of insulin secreted into the blood stream, thereby causing a deficiency of active insulin. L. W. RIGGS

Excretion of certain nitrogenous substances in the urine in the course of experimental nephritis. JOHN MOSONYI. *Magyar Orvosi Archivum* 26, 244-7(1925).—A dog poisoned with U showed a diminution in the excretion of carbamide, preformed ammonia and creatinine. After regeneration of the kidney the excretion of creatinine reaches its normal amt much later than the other substances. The increase of N excretion, elsewhere stated to occur in the course of U-nephritis, could not be confirmed. L. W. RIGGS

Experimental production of malignant growths by simple chemicals. J. K. NARAY. *J. Cancer Res.* 9, 135-47(1925).—Repeated applications of HCl and KOH and tar to the skin of mice over prolonged periods resulted in the production of papillomatous and ulcerative lesions. Some strains of mice were refractory to the exptl. production of cancer, while in others the application of KOH or HCl elicited formation of tumors which presented morphologically as well as biologically the characteristics of cancer. F. B. SEIBERT

The metabolism of carcinoma cells. OTTO WARBURG. *J. Cancer Res.* 9, 148-63(1925); cf. *C. A.* 19, 1159, 2370.—A review of the German literature. F. B. S.

The acidic value of the urine in skin and other manifestations. F. C. DOATE. *Lancet* 1925, I, 272-4.—In some 500 cases of patients suffering from skin diseases, all of those with seborrhea, seborrheic eczema, acne, and cheilopompholyx had a urine with a pH value of from 4.8-5.8. The disease usually cleared up when alkalis were administered and the pH of the urine approached normal. Also in *J. Roy. Army Med. Corps* 45, 29-35. F. B. SEIBERT

The renal threshold for glucose. E. WORDLEY. *Lancet* 1925, I, 655-6.—Ten cases of diabetes associated with renal disease are described, and in all there is present a marked inability to conc. urea as judged by MacLean's urea-concn. test. In 8 of these cases the renal threshold for glucose was normal and in 2 it was raised. It appears that chronic nephritis of the azotemic types does not, in the majority of cases, alter the permeability of the kidney for glucose. The MacLean test of urea concn. is of greater value in estg. the function of the kidney in diabetes than an estn. of the blood urea. F. B. SEIBERT

The experimental production of cancer by one application of tar. G. M. FINDLAY. *Lancet* 1925, I, 714-5.—A small percent of mice receiving a single application of hot tar to the skin developed epitheliomata resembling those produced by long-continued treatment. F. B. SEIBERT

Colloidal kaolin. I. Some properties of colloidal kaolin. W. J. POPE AND T. M. HAYNES. *Lancet* 1925, I, 1123-4.—A clay, more finely divided than usual, was employed in these expts. When shaken with H<sub>2</sub>O it remains in suspension for a week. The addn. of 0.3% HCl or 1.3% NaCl causes flocculation. It is not flocculated by moderate amts. of NaOH. It is a negative colloid and causes flocculation with positive colloids, such as FeCl<sub>3</sub>. It is partially adsorbed by kaolin and basic dyes are not completely removed from soln. but become distributed between the soln. and the kaolin in proportions which can be detd. II. The absorption of toxin by kaolin. J. W. II. HYKE. *Ibid* 1124-5.—When diphtheria toxin is filtered through kaolin plus agar the toxicity is not reduced even to the extent of 6-min. lethal doses, while kaolin alone adsorbs about 5-min. lethal doses. These results could not be repeated with *B. dysenteriae* toxin. F. B. SEIBERT

Estimation of the clinical value of the van den Bergh test. ELIZABETH G. RAVDIN. *Am. J. Med. Sci.* 169, 850-60(1925).—The estn. of the type and quantity of bilirubin in the blood serum (van den Bergh test) in a series of 100 cases gave results in accord with the clinical picture, differentiating consistently between the jaundice of obstruction and of hemolysis. The tests are tests for liver function only insofar as they indicate alteration in bile pigment metabolism. G. H. S.

Thyroxin and tryptophan content of the diseased thyroid gland, and the iodine compounds in desiccated thyroid. J. F. WEIR. *Am. J. Med. Sci.* 169, 860-5(1925).—From the synthetic work with thyroxin, it appears impossible to alter any compd. which could be called a precursor of thyroxin into thyroxin by treatment with alkali. In the normal gland the quantity of total I present in a form stable to NaOH (thyroxin) is approx. 50% of the total I. In exophthalmic goiter the total quantity of I present is less than normal, and the percentage of the total which is in the form of thyroxin is very materially reduced. After administration of Lugol's soln. the total quantity of I in the exophthalmic goiter increases, as does the % of thyroxin; these changes parallel the clinical improvement. There is no apparent relationship between the thyroxin content of the thyroid and the basal metabolic rate. Tryptophan exists in the thyroid in a rather high percentage, av. 3%, but no definite relation was found between this and the pathol. type of gland, the thyroxin content, or the basal metabolic rate. The I which is sol. in acid after the gland has been digested with NaOH is not present as inorg. iodide, but is still organically combined. G. H. S.

Value of the estimation of the ionic calcium of the serum in the diagnosis of, and as a gage of progress in sprue. H. H. SCORR. *Ann. Trop. Med.* 19, 23-35(1925).—In sprue the total quantity of Ca in the serum remains approx. normal, but there is a regularly observed fall in the quantity of ionic Ca, the fluctuations in value of which coincide with clinical changes. Absorption of Ca is little, if at all, interfered with in sprue, but the Ca metabolism is upset, a condition probably referable to disturbed parathyroid function. Cure in sprue is obtained by oral administration of suitable salts of Ca and parathyroid prepn. G. H. S.

Agglutinin formation following the use of Castellani's glycerovaccine. CRISTOBAL MANALANG. *Philippine J. Sci.* 26, 317-20(1925).—A single injection of the glycerovaccine results in the development of agglutinins for *V. cholerae* to a higher titer than do several injections of a saline vaccine. The glycerovaccine is multivalent (cholera-typhoid-paratyphoid A and B). Agglutinins for the cholera vibrio appeared in 37 of 43 persons injected, usually between the 9th and 14th days. In the majority of cases the titer had fallen to below 1:20 within 160 days after the injection. G. H. S.

Tuberculin and protein sensitivity of the skin. EDMUND NOBEL AND ALEXANDER ROSENBLUTH. *Z. Kinderheilk.* 39, 439-47(1925).—Cutaneous sensitivity of albumose-free tuberculin is less than to old tuberculin (Koch). With the intracutaneous test all children which react positively to old tuberculin give also a positive reaction with the albumose-free prepn. Although tuberculin-positive children may react to protein-free substances they react much more strongly to protein materials. Many tuberculin-positive children, reacting positively to intracutaneous administration of albumose-free media, reacted also to the cutaneous introduction of bouillon. G. H. S.

## H—PHARMACOLOGY

ALFRED N. RICHARDS

Insulin and the oxidation of dextrose. G. AHLGREN. *Berl. klin. Wochschr.* 3, 1158-60(1924).—Finely divided frog muscle in the presence of methylene-blue oxidizes dextrose only over a certain range of concn. of insulin ( $10^{-9}$  to  $10^{-12}$ ). At higher concns., oxidation of dextrose is inhibited. The muscle must be examd. immediately after removal from the body in order to detect the glycolysis induced by insulin during life. B. C. A.

Insulin. II. J. A. COLLAZO, M. HÄNDEL AND P. RUBINO. *Deut. med. Wochschr.* 50, 747-8(1924); cf. C. A. 18, 1858.—The glycogen content of the liver and muscle of guinea pigs to which 3 g. of dextrose and then insulin have been administered, and which show hypoglycemia without convulsions, is 50-70% above normal. Insulin *in vitro* does not cause a synthesis of glycogen. In minced muscle (guinea pig, dog and rabbit), in the presence of  $\text{NaHCO}_3$  at 35°, an appreciable increase in the production of lactic acid is observed within 2 hrs., accompanied by an increase in inorg. P. The decompn. of lactic acidogen is thus promoted by insulin. The seat of the action of insulin is held to be in the muscles. B. C. A.

Insulin and its action. III. Lactic acid content of muscle in death due to insulin or to starvation. H. BAUR AND R. KÜHN. *Münch. med. Wochschr.* 71, 541-4(1924); cf. Baur, Kuhn and Wacker, *Münch. med. Wochschr.* 71, 187(1924).—The lactic acid content of the skeletal muscle of rabbits killed by insulin is less than that of normal animals and does not exhibit the usual post-mortem rise. Lower figures still are obtained for the lactic acid content of the muscles of animals killed by starvation. B. C. A.

Resorption of bismuth in relation to bismuth intoxication. G. FRITZ *Omnis Helvæ* 67, 333-5(1923).—Dipotassium bismuthotartrate in 5% soln (Richter's bismulol) injected intravenously (0.01 g. of Bi per 1 g. body-weight) is fatal to rabbits (convulsions, dyspnea and cardiac paralysis). When this compd. is administered intramuscularly suspended in olive oil, resorption takes place rapidly, and in 8 to 10 days after administration of 0.05-0.1 g. of Bi, the urine is free from Bi. Resorption is slower and more irregular from a paraffin oil suspension. In its action on urine, the Bi, after oxidation with  $\text{KClO}_3$  and  $\text{HCl}$ , is pptd. as sulfide, and, after soln. of this in  $\text{HNO}_3$ , is pptd. and weighed as oxalate (dried to const. wt. at  $60^\circ$ ). B. C. A.

Chaulmoogra and margosa oils together with a contribution to heterogeneous catalyzers. F. NORD AND G. G. SCHWEITZER. *Biochem. Z.* 156, 269-77(1925).—Chaulmoogra oil, margosa oil and the mixed fatty acids from chaulmoogra oil, preps. that have shown physiol. action in the treatment of leprosy, were hydrogenated.  $\text{PdCl}_2$  and Ni were used as catalyzers. The decrease in I no. was, in the case of the optically active oils, accompanied by a decrease in optical rotation. It is concluded that there is a relation between optical activity and physiol. action and that the latter is independent of the cyclic structure of chaulmoogric or hydrocarpic acids. F. A. CAYORI.

Ion action on the heart. F. HOFMANN. *Biochem. Z.* 156, 278-86(1925).—A review and discussion of the action of Ca, K and Na ions on the regularity of the heart beat. F. A. C.

Adsorption phenomena in the toxicology of hydrocyanic acid. A. CERVALLI. *Arch. ital. biol.* 73, 61-4(1924).—When HCN is drawn through a tube contg. 1.8 g. wool, this after treatment with 31 000 l. air during 15 min. still retains sufficient HCN to kill in 10 min. a guinea pig enclosed with it under a bell jar. A. T. CAMERON.

*Ananias citrina* Pers. and *Mappa Batsch* and their toxicological position. V. PETTINARI. *Boll. soc. med. chir. Pavia* 36(1923), *Arch. ital. biol.* 74, 81(1924).—They contain no other volatile, toxic, thermostable substances than a hemolytic principle, and this hemolysin is present only in a small quantity. A. T. CAMERON.

Absorption, elimination, and toxicity of cinchonine. S. SILVESTRI. *Polidm. sc. med.* 30, 601(1923), *Arch. ital. biol.* 74, 81-2(1924).—Guinea pigs absorb cinchonine more rapidly than quinine, and on this account it is more toxic to them. A guanine cinchonine mixt. is more toxic than an equiv. quantity by wt. of either. Cf. C. A. 18, 3085. A. T. CAMERON.

Action of acetylene. VI. Comparative studies on the sensitivity of cold- and warm-blooded animals toward acetylene. KARL FUERST. *Z. physiol. Chem.* 144, 78-9(1925).—With mice the liminal concn. of  $\text{C}_2\text{H}_2$  in the blood at body temp. of about  $39^\circ$  for narcosis is practically identical with that of fish at room temp. of  $18.5^\circ$ , the a.v. value being about 39.5 vol. % in both cases. A. W. DOX.

A biological proof of the taking-up of cations by the red corpuscles of the rabbit. C. HEYMA. *Arch. intern. pharmacodynamie* 28, 437-43(1924); *Physiol. Abstracts* 9, 294.—The perfused isolated heart of the frog provides a suitable test-object to est. concns. of Ca or K ions.  $\text{CaCl}_2$  and  $\text{KCl}$  solns., which have been in contact with rabbit red corpuscles, show less effect on the heart than control solns. H. G.

Pharmacological researches on the active principle of liquorice. Is the active principle of liquorice a substance of the saponin group? L. TOCCO-TOCCO. *Arch. intern. pharmacodynamie* 28, 445-54, 455-66(1924); *Physiol. Abstracts* 9, 348.—Glycyrrhizin has a toxic action on unicellular organisms and on fishes. It has also a hemolytic action. In many of its phys., chem., and pharmacol. properties it resembles the saponins, but it has not yet been decided whether it should be included in this group. H. G.

Fixation of calcium by adrenaline. L. PINET AND M. VAGLIANO. *J. méd. de Bordeaux* 14, 585(1924); *Physiol. Abstracts* 9, 542-3.—Injection of adrenaline diminishes the content of Ca in the blood. It is uncertain whether the hypocalcemia means actual diminution of the Ca in the organism or fixation in some other form. Adrenaline was shown to have a curative effect on rats suffering from rickets. Adrenaline is a fixing agent of Ca. H. G.

The influence of physical conditions on the action of drugs. I. The influence of heat. S. INOUE. *Acta Schol. Med. Univ. Imp. Kioto* [II], 6, 261-73(1923).—Although an increase in temp. is followed by an increase in drug (atropine, phocarpine, caffeine, EtOH, camphor,  $\text{BaCl}_2$ ) activity on isolated frog hearts there is no direct proportionality between these two factors. Changes in state of the heart (exhaustion, etc.), with temp. increase probably influence variations in drug activity as does the greater frequency of heart beat. W. F. GOEBEL.

The fate of benzylamine in the animal organism. T. IMAI. *Acta Schol. Med. Univ. Imp. Kioto* [IV], 6, 415-9(1924).—From the urine of chickens which had received

subcutaneous injections of 3.0 g.  $\text{PhCH}_2\text{NH}_2 \cdot \text{HCl}$  (I) in daily doses of 0.75 g., approx 0.3 g. of ornithuric acid and 0.10 g. of  $\text{PhCOOH}$  could be recovered. From the urine of dogs similarly treated with daily doses of 1.0 g. of I varying amts. of hippuric acid were obtained.

W F GOEBEL

The fate of quinoline in the animal organism. I. S TAMURA. *Acta Schol. Med. Univ. Imp. Kioto* [IV], 6, 449-54 (1924).—From the urine of dogs which had received subcutaneous injections of 9.5 g. quinoline (dissolved in olive oil) in daily doses of 0.4 g. methylquinolinium hydroxide (I) was isolated as its Pt salt. Similar expts with rabbits gave quantities of I too small to be isolated. II. *Ibid* 455-60.—Quinoline (in olive oil soln.) when injected subcutaneously into rabbits and dogs is partially oxidized and is excreted in the urine paired with  $\text{H}_2\text{SO}_4$  and glucuronic acid. W F G.

The fate of methylquinolinium hydroxide in the animal organism. S TAMURA. *Acta Schol. Med. Univ. Imp. Kioto* [IV], 6, 459-60 (1924).—Methylquinolinium hydroxide is excreted unchanged in the urine of rabbits, dogs and chickens when given subcutaneously. It is far less toxic than quinoline and can be given in doses of 1 g. with no harmful effects.

W F GOEBEL

Experimental studies on the effects of diuretics in the intravenous infusion of Ringer-Locke solution. I. TSURUMAKI. *Acta Schol. Med. Univ. Imp. Kioto* [VI], 6, 151-67 (1923).—The intravenous injection of theobromine Na salicylate or caffeine during the infusion of Ringer-Locke soln. increases urine output. Repeated injection increases the fatal infusion quantity. The effect of cardiotonics (adrenaline, camphor) on the increase in fatal infusion quantities of Ringer-Locke soln. is still in doubt.

W F GOEBEL

The difference in biological action between  $\alpha$ - and  $\beta$ -phenylethylamine. I. MATSUO AND H. MIZUNO. *Acta Schol. Med. Univ. Imp. Kioto* [I], 7, 11-20 (1924).— $\text{CH}_3\text{CHPhNH}_2$  (I) contracts the blood vessels of the rabbit ear more than  $\text{PhCH}_2\text{CH}_2\text{NH}_2$  (II) does. I increases the contraction amplitude of the frog heart and the blood pressure of a rabbit, II shows the opposite effect. In the spontaneous movements of the frog stomach I and II both show an increase of contraction amplitude; the action I is much stronger than that of II.

W F GOEBEL

The beneficial effects of barium chloride on Adam-Stokes disease. A. E. COHN AND S. A. LEVINE. *Arch. Intern. Med.* 36, 1-12 (1925).—In 3 patients with complete heart block, in whom the customary procedures did not give relief, the administration of 30 mg.  $\text{BaCl}_2$ , 3 or 4 times a day, by mouth promptly increased the irritability of the ventricles and prevented the long asystolic periods, thus rendering the patients free from attacks.

I GREENWALD

Neutral-salt skin reactions. I and II. SIGWALD BOMMER. *Klin. Wochschr.* 3, 1758 (1924); 4, 1208-9 (1925).—All K salts produce a painful burning sensation when injected intradermally. The effect is most pronounced with  $\text{K}_2\text{SO}_4$ . Of the Na salts, only  $\text{Na}_2\text{SO}_4$  produces a slight burning sensation. This reaction is characteristic of the K and SO<sub>4</sub> ions; but is most pronounced for K. The welt produced with K salts becomes bright red in 3-4 minutes and remains red for 20 minutes. Injections with Ca salts are not painful. They produce a prominent, yellow exudation welt with tensely stretched skin, sharply defined edges and an intensely red border. A serous fluid finally oozes from the point of puncture. Mg salt injections are not painful. The welt is rapidly absorbed. Mg decreases the burning sensation due to the K ion, and  $\text{MgSO}_4$  does not produce a burning sensation.

MILTON HANKE

The action of cations in parathyroid tetany. S HIRSCH. *Klin. Wochschr.* 3, 2284-5 (1924).—Administration of Sr salts removes the clinical symptoms of parathyroid tetany. The effects are instantaneous after intravenous injection; but are quite as satisfactory, though less rapid, after peroral administration.

MILTON HANKE

Chemical changes in the blood induced by a pharmacological stimulation of the vagus. HERMANN VOLLMER. *Klin. Wochschr.* 3, 2285-7 (1924).—Injection of pilocarpine leads to an increase in the concn. of serum proteins due to a dehydration of the blood. Ca is increased in percent; but when allowance is made for blood dehydration, Ca is actually decreased 0.291 mg. % K is increased in proportion to the dehydration. Choline has no const. effect upon blood hydration. Ca and K are unchanged. Pharmacological stimulation of the vagus does not lead to any marked changes in the Ca or K concn. of the blood.

MILTON HANKE

The blood-pressure reaction in normal and in parathyroidectomized dogs. DANIEL ALPERN. *Klin. Wochschr.* 4, 551 (1925).—In normal animals injecting acid or alkali has no effect upon the adrenaline reaction.  $\text{CaCl}_2$ ,  $\text{KCl}$ ,  $\text{MgCl}_2$  and especially  $\text{NaCl}$  reduce the intensity of the adrenaline reaction when they are injected with the adrenaline.  $\text{NaHPO}_4$  prolongs the action of adrenaline and may intensify it. Severing the

neck vagi does not change the effect of the electrolytes on the adrenaline reaction. In parathyroidectomized animals in that stage of tetany where the Ca content of the blood is normal and the alkali reserve low, adrenaline elicits its normal reaction. With low Ca and normal alkali reserve, adrenaline reaction is markedly reduced or may be negative.  $\text{HCl}$  or  $\text{CaCl}_2$  elevates the reaction but never to normal.  $\text{Na}_2\text{HPO}_4$  is without effect.

MILTON HANKE

The role of the liver during insulin hypoglycemia. LUIGI VILLA. *Klin. Wochschr.* 4, 551-2(1925).—Insulin reduces the blood sugar more in the vena cava and vena femoralis than in the hepatic vein. Hypoglycemic symptoms are associated with blood sugar values (vena cava) below 0.045%. Blood from the hepatic vein contains more than this minimum value of glucose except during the very severe cramp period, when the values are almost identical for both veins. Adrenaline in the vena cava promptly removes convulsions; the blood sugar slowly rises to normal within one hr. Adrenaline in the portal vein leads to a hyperglycemia in the hepatic vein within a few minutes. Doses of adrenaline that would ordinarily be fatal, are tolerated perfectly by hypoglycemic animals. Insulin induces hypoglycemia by inhibiting the conversion of glycogen to glucose. Adrenaline removes this inhibitory action.

MILTON HANKE

Significance of the calcium ion for nervous excitability. HANS HANDOVSKY AND C. C. FONO. *Klin. Wochschr.* 4, 1123(1925).—Caffeine acts as a nerve excitant regardless of the compn. of liquid in which the muscle nerve prepn. is suspended. Urethan is a nerve excitant at low concns. (1:35,000) and paralyzes at higher concns. The excitability of nerves is increased by K ion and decreased by Ca ion.

M. H.

The mechanism of motor innervation of the stomach. YOSHISADA NAKASHIMA. *Klin. Wochschr.* 4, 1214(1925).—Gastric muscle tonus is increased (ape and dog) when certain concns. of adrenaline are injected, decreased with higher concns. Extravasations, erosions and ulcers are not produced. The latter are obtained only when adrenaline and pilocarpine are simultaneously injected in suitable concns.

MILTON HANKE

Diuretic action of bismuth salts. A. L. MOLNAR. *Klin. Wochschr.* 4, 1267(1925).—Bi salts are almost as diuretic as Hg salts. Their much lower toxicity makes them valuable in the treatment of edema.

MILTON HANKE

Action of inorganic salts on the secretion of the isolated kidney. F. EICHENOLTZ AND E. H. STARKING. *Proc. Roy. Soc. (London)* 98B, 93-113(1925).—Ca working on a background of K increases the excretion of  $\text{H}_2\text{O}$  and chlorides by decreasing the reabsorption in the tubules, the salts of these metals, administered separately, have no definite effects. Inorg. phosphates convert the Ca ion into a colloidal compd., and thereby decrease the excretion of  $\text{H}_2\text{O}$  and chlorides. The glomerular membrane is impermeable to the colloidal phosphates, but is rendered permeable to them by cyanides.

JOSEPH S. HEPBURN

The therapeutic use of dehydrocholic acid in febrile diseases of the bile passages. D. ADLERSBERG AND E. NEUBAUER. *Wiener Arch. inn. Med.* 10, 59-70(1925).—Intravenous injection of 2 g. of the Na salt of dehydrocholic acid greatly increases the secretion of bile. Clinical use was made of this in selected cases of cholecystitis and cholangitis with favorable results in 6 of the 7 cases.

HARRIET F. HOLMES

Experimental influencing of the residual nitrogen of the blood by intravenous injections of urea. IMRE SCHILL AND J. KUNZE. *Wiener Arch. inn. Med.* 10, 329-38(1925).—After intravenous injections of urea, the residual N of the blood and urine was detd. at various intervals. The urea disappeared from the blood very rapidly in the first few min., and then more slowly. As in 2 or 3 days there was no appreciable increase of urea excretion in the urine, it is probable that the urea is bound by the tissue cells.

HARRIET F. HOLMES

Experimental study of the mechanism of the action of insulin. G. HEYNYL. *Z. ges. expil. Med.* 45, 439-51(1925).—Insulin injections in rabbits is followed by a decrease in the sugar content of the blood, then of the organs with the exception of the liver, and later of the liver. In the so-called hypoglycemic complex the blood and organ sugar content are very low, while the sugar content of the liver rises rapidly. Adrenaline, which brings the animals out of convulsions or coma, causes a decrease in the sugar content in the liver and an increase in the blood and organs. It is probable that a hormone from the pancreas regulates the correlation of sugar content of the liver and other tissues.

HARRIET F. HOLMES

Is the swelling in vitro of kidney cortex and medulla actually influenced by caffeine? N. W. LAZAREW AND M. A. MAGATH. *Z. ges. expil. Med.* 45, 475-8(1925).—Expts. in vitro on the action of caffeine on cortex and medulla of the kidneys of rabbits gave no ground for explaining the diuretic action of caffeine through a direct influence of caffeine on the binding of  $\text{H}_2\text{O}$  by kidney tissue.

HARRIET F. HOLMES

**Leprosy. XXXVI. Treatment of leprosy with derivatives of chaulmoogra oil.** H. E. HASSELTINE. U. S. Public Health Service, *Bull.* 141, 1-11(1924).—The mixed Et esters of the fatty acids of chaulmoogra oil contg. 1% of I have proved the best therapeutic agent in leprosy. The mixed esters gave better results than those of chaulmoogric, hydnocarpic and acid M alone. Acid M is a mixt. of acids with a high I value. The Bu esters have no advantage over the Et esters. The esters of the purified acids are preferable to the crude oil or its emulsions as their injections are far less painful. Intramuscular injections are more efficient than intravenous. The I prevents local irritation and discomfort. **XXXIX. Treatment of leprosy with compounds of antimony.** H. E. HASSELTINE AND P. J. GORMAN. *Ibid.* 28-30, cf. *C. A.* 19, 2476. —In a group of 10 lepers treatment with colloidal Sb resulted in a hardly perceptible improvement in the anesthetic type, and had no effect on lesions or acid-fast bacilli in the nodular and mixed type. MARY JACOBSEN

**Surgery in the treatment of bronchial asthma.** HUGO HABICHER. *Am. Med.* 31, 366-7(1925).—Discussion showing the shortcomings of surgery in this connection and the benefits of anti-allergic therapy, adrenaline and phospho-cod-liver oil. F. K.

**The role of radiotherapy in chronic infections.** IRA O. DENMAN. *Am. Med.* 31, 367-70(1925).—Discussion showing the efficacy of radiotherapy. F. KRASNOW

**The effect of the administration of iodine on exophthalmic goiter.** A. S. JACKSON. *Ann. Surgery* 81, 739-48(1925).—After several weeks, a tolerance to I is developed and its efficacy is diminished. FRANCES KRASNOW

**The elimination of morphine and other accessory drugs in operations under local anesthesia.** J. GORDON ANDERSON. *Ann. Surgery* 81, 994-1001(1925).—The pre-operative administration of morphine and adrenaline is not as beneficial as has been generally believed; this is particularly true in urological cases. "In the majority of cases, local anesthesia, properly administered, affords the patient the desired relief from pain." FRANCES KRASNOW

**Fluoride poisoning.** RAESTRUP. *Deut. Z. ges. ger. Med.* 5, 406-14(1925).—Discussion. FRANCES KRASNOW

**Death due to careless injection of adrenaline.** ERNST ZIEMKE. *Deut. Z. ges. ger. Med.* 5, 515-31(1925).—Case reports and discussion. FRANCES KRASNOW

**Arsenic poisoning.** LÜHRIG. *Deut. Z. ges. ger. Med.* 5, 543-52(1925).—Case report. FRANCES KRASNOW

**Chemotherapy of antimonial compounds in kala-azar infection. III. Further observation on dermal leishmanoid.** H. E. SHORTT AND U. N. BRAHMACHARI. *Indian J. Med. Research* 12, 463-6(1925); cf. *C. A.* 19, 872.—Report of a case of leishmaniasis skin infection which required prolonged treatment and showed very slow improvement. FRANCES KRASNOW

**Notes on the concentrations of anticobra serum. IV. Absorption spectrum.** J. F. CAUS AND A. STEICHEN. *Indian J. Med. Research* 12, 499-502(1925); cf. *C. A.* 19, 106.—The absorption spectra of normal horse serum and antivenomous horse serum are identical. FRANCES KRASNOW

**Studies on lathyrism.** L. A. P. ANDERSON, A. HOWARD AND J. L. SIMONSEN. *Indian J. Med. Research* 12, 613-45(1925).—Chemical examn. of the seeds of khesari (*Lathyrus sativus* L.) shows them free from colloidal substances. Feeding expts. with ducks and monkeys have demonstrated that they are harmless and provide a nourishing diet. The weeds contaminating khesari (*Vicia sativa* L. or akta) contain colloidal bases. Vicine, divicine and the cyanogenetic glucoside vicianin have been isolated. "Divicine, which occurs in akta in combination with a sugar as the glucoside vicine, produces on inoculation in guinea pigs a characteristic and fatal disease. Akta, when fed to ducks, causes death; in monkeys it produces a very characteristic train of symptoms affecting the nervous and muscular systems." Although there is some likeness of these systems to human lathyrism, specific proof is lacking. FRANCES KRASNOW

**The quantity of urea stibamine, "471" (von Heyden) and stibamine glucoside required for the complete treatment of a case of kala-azar.** E. D. W. GREIG AND S. KUNPU. *Indian J. Med. Research* 12, 679-83(1925).—The three drugs seem to show equal efficiencies although only few cases have been treated with stibamine glucoside. The quantities used in g. per kg. body wt. are for urea stibamine 0.053, "471" 0.00, stibamine glucoside 0.042. FRANCES KRASNOW

**Chemotherapy of antimonial compounds in kala-azar infection. XIV. Observations on a series of cases of kala-azar treated with urea stibamine during a course of 32 hours to 7 days.** U. N. BRAHMACHARI AND B. B. MAITY. *Indian J. Med. Research* 12, 735-40(1925).—Intensive method of giving multiple injections on the same day in order to maintain a concn. of urea stibamine in the blood has remarkably short-

ened the period required for sterilization. The time required for complete cure varies in different individuals and ranges from 32 hrs. to 7 days. FRANCIS KRASNOW

The effect of formalin on snake venom. I. Diminution of toxicity of cobra venom. C. DE C. MARTIN. *Indian J. Med. Research* 12, 807-10 (1925).—Formalin decreases the toxicity of cobra venom for pigeons; the action is accelerated by temp. increase. FRANCIS KRASNOW

The effect of cod-liver oil on dogs convalescing from distemper. A. S. SCHLINGMAN. *J. Am. Vet. Med. Assoc.* 67, 91-7 (1925).—Cod liver oil is of great benefit in shortening the period of convalescence. FRANCIS KRASNOW

Progress of leprosy treatment work at Cullion leper colony. JOSE RODRIGUEZ. *J. Philippine Islands Med. Assoc.* 5, 40-6 (1925).—2810 patients received treatment. Of the preps. used (ethyl esters of chaulmoogra oil with 0.5% iodine; ethyl esters with 10% creosote; ethyl esters with 0.5% iodine and 10% creosote; Mercado mixt.) the iodized ethyl esters continued to give the best results. FRANCIS KRASNOW

Results obtained from the various treatments of leprosy at San Lazaro Hospital, 1920-1924. CATALINO GAYINO AND SAMUEL TIETZE. *J. Philippine Islands Med. Assoc.* 5, 50-61 (1925).—The chaulmoogra oil ethyl esters with 0.5% iodine produced the quickest improvement. This treatment is easiest in technic and gives least discomfort to the patient. FRANCIS KRASNOW

A study of intensive antimony therapy in schistosomiasis japonica. H. E. McLENEY, E. CARROLL FAUST AND C. M. WASSILL. *J. Trop. Med.* 28, 153-6 (1925).—Treatment of moderately advanced cases with tartar emetic gave evidence of marked improvement and probable cure as indicated by clinical and lab. exams. F. K.

Beneficial action of raw pancreas in certain cases of sprue. Insulin in cases of sprue complicated with diabetes. ALDO CASTELLANI. *J. Trop. Med.* 28, 230-1 (1925).—Administration of raw pancreas seems beneficial when used in addition to the alkaline and milk treatment. Insulin induced disappearance of glucosuria but had no effect on the sprue symptoms. FRANCIS KRASNOW

Insulin and diabetes. R. JAKSCH-WARTENHORST. *Centr. inn. Med.* 45, 1-3 (1924).—The author testifies as to the curative action of insulin in cases of diabetes mellitus ranging in severity from diabetic coma to a very slight glucosuria. The quantity of insulin necessary can be minimized by a previous dietetic treatment. Polyglandular disease with diabetes is not cured with insulin. In severe diabetes as much as 100 units per day has been given. JULIAN H. LEWIS

Sodium nitrite injections in disturbances of blood vessel innervation. EUGEN NAGY. *Centr. inn. Med.* 45, 69-73 (1924).—Subcutaneous injections of  $\text{NaNO}_2$  give better results in the treatment of dysbasia intermitten and angina pectoris than any other substance. They are also useful in the treatment of nephritis, nephrosclerosis and arteriosclerosis. A marked fall in blood pressure which lasts for several hrs. is produced. JULIAN H. LEWIS

Calcium in myocardial weakness. PAUL ENGELN. *Centr. inn. Med.* 45, 149-51 (1924).—Cases of constitutional circulatory weakness in which there is an abnormal irritability of the heart, of myocardial weakness associated with heart valve disease and cases of myocardial insufficiency which do not respond well to digitalis are markedly improved by treatment with Ca. JULIAN H. LEWIS

The influence of insulin on the inorganic and organic phosphates of the liver. C. F. CORI AND HILDA L. GOLTZ. *Am. J. Physiol.* 72, 256-9 (1925).—The decrease in the free sugar of the liver, commonly observed during insulin action, is not due to the formation of a hexosephosphoric acid complex in that organ. J. F. LYMAN

Deceptive effects of extracts of suprarenal cortex. Cardiac effect produced by potassium content; intestinal effects due to epinephrine and choline. O. W. BARLOW AND T. SOLLMANN. *Am. J. Physiol.* 72, 343-6 (1925).—Alec. exts. of the suprarenal cortex produce a striking heart block when perfused through frog hearts, due to the K extd. from the tissue. Intestinal movements are depressed by the exts. because of the traces of adrenalin. When this is removed by oxidation a moderate choline stimulation becomes apparent. J. F. LYMAN

Anticoagulant action of zinc salts. AUGUSTE LUMIERE AND HENRI COUTURIER. *Compt. rend.* 180, 1364-6 (1925); cf. *C. A.* 19, 1907.— $\text{ZnSO}_4$  in a concn. of 1 to 2,000 prevents completely the coagulation of blood *in vitro*. An injection of 5 mg.  $\text{ZnSO}_4$  per kg. of body wt. into the circulation of the guinea pig causes a slight stupor and the coagulation of the blood is sufficiently retarded so that there is no danger of obstructing the capillaries or the registering app. with clots. Salts of Ca added to blood made uncoagulable by  $\text{Zn}^{++}$ , do not restore the property of coagulability as they do with oxa-

lates and citrates, this shows that the mechanism of these is different from that of  $ZnSO_4$ . I. W. RUSK.

**Action of insulin on nitrogenous metabolism.** H. LAMM AND B. THOMPSON. *Compt. rend.* 180, 1538-40(1925). Normal dogs under a diet which maintained const. body wt. and N equil., were given by injection from 15 to 15 cubic cm. of insulin, or a max. of about 5 units per kg. of body wt. The dogs with 2 of the dogs covered periods of 33 and 37 days, resp. Two insulin periods sep. by a month's interval were observed with the 3rd dog. Following the injection of insulin the total N was always increased and the wt. of the animal was decreased. I. W. RUSK.

**Action in vitro of pancreatic extracts on the trypanosome of nagana and on the *Sprocheta gallinarum*.** CLEMENT SIMON, CH. FLANDIN, SLODIN AND LÉVY. *Compt. rend.* 180, 1541-2(1925). A sample of insulin prep. by extn. of pancreas with acidified alc., and purified by recovery from the plate, killed the trypanosome of nagana in 30 to 35 min. at a temp. of 25° and a diln. of 1 to 100. Comparable results were obtained by treating *Sprocheta gallinarum* with the same medium. The stock insulin soln. had a concn. of 1 to 50 and a pH 4.0. Neutral solns. containing the insulin as a ppt. in suspension were toxic to the above-mentioned organisms in a diln. of 1 to 300. If the insulin ppt. was dissolved in the min. amt. of NaOH the soln. appeared to lose its trypanocidal properties. I. W. RUSK.

**Inorganic phosphates and insulin hypoglycemia.** A. DEMOZ, H. HENRY AND P. RATHNY. *Compt. rend.* 180, 1551-7(1925). Dogs were given subcutaneous injections of 10 or 20 mg. of insulin (a given animal always receiving insulin from the same pancreas) and followed immediately by an intravenous or subcutaneous injection of a soln. of 2 to 4.2 g. of a mixt. of  $Na_2HPO_4$  and  $KH_2PO_4$  adjusted to a pH of about 7.4. The sugar content of the plasma was stud. before and at various periods after the injections. The results proved that the injection of the phosphates intensified and prolonged in a remarkable manner the hypoglycemia produced by the insulin. I. W. RUSK.

**Two deaths from the administration of barium salts.** WM. D. McNALLY, J. Am. Med. Assoc. 84, 1805-7(1925). The toxicology of  $BaCl_2$  is described. "Barium given to patients for Röntgen ray exam. should be a c. p. grade and be given by the person who is to make the exam. Each lot of  $BaSO_4$  should be tested for acid. impurities." I. W. RUSK.

**Fungicidal activity of certain oils and atraroptena.** H. B. MYERS AND C. H. TURNER. J. Am. Med. Assoc. 84, 1805-6(1925). Twenty hour lit. cultures in meat broth of a yeast-like organism which had been responsible for occupational dermatitis were destroyed by the official H. P. assay of the volatile oils of thymol and cinnamon more readily than by 1% phenol. The drugs mentioned caused immediate improvement towards healing of infections apparently due to fungal organisms of several types. Clove, menthol, peppermint, eucalypt, Mr. salicylate, turpentine, eucalyptus, turpene and lemon had less fungicidal power than 1% phenol but oil of cloves was nearly as efficient. I. W. RUSK.

**Influence of narcotics upon the surface tension.** PETRUS CZANIK. *Magyar Orvosi Archivum* 26, 255-63(1925). The pharmacol. action of paralyzing and irritating substances cannot be attributed to their action upon the surface tension. While the substances decrease the surface tension, such action affects only the penetrating power into the cell, in which the actual pharmacol. action must arise from sp. chemical actions. I. W. RUSK.

**Factors in the selection of an anthelmintic.** F. L. FOWLER. Am. J. Hyg. 5, 408-53(1925).—Oil of chenopodium and  $CCl_4$  both possess a species and sex selective action on *Necator* and *Ankylostoma*. Both are more effective against *Necator*, oil of chenopodium being more active toward males than females,  $CCl_4$  more active for females than for males. Simultaneous administration of concn.  $MgSO_4$  with combinations of  $CCl_4$  and oil of chenopodium delays the expulsion of worms but does not impair the ultimate anthelmintic results. In *Necator* treatment 1 cc. of a 2:1 mixt. of  $CCl_4$  with simultaneous  $MgSO_4$  is very efficient. For *Ankylostoma* the best results are obtained with 2 cc. of a mixt. (1.8 cc. of  $CCl_4$  with 1.0 cc. of oil of chenopodium). G. H. B.

**Magnesium sulfate with special reference to its use in biliary drainage.** H. W. SARK. Am. J. Med. Sci. 109, 374-407(1925). The therapeutic effect of  $MgSO_4$  in biliary drainage is essentially the same whether administered by mouth or by duodenal tube, there being no chem. evidence to indicate that the coln. differs in any way when it reaches the duodenum when it is given one way or the other. Probably the only change in the coln. to take place in its passage through the stomach is a concn. G. H. B.

Electrocardiographic studies of the effects of ether upon the living cat's normal heart. H. R. MILLER, DAVID FELBERBAUM AND H. T. KRIGEL. *Am. J. Med. Sci.* 169, 516-31(1925).—With adequate changes in the depth and duration of ether anesthesia cardiac abnormalities occur promptly but the irregularities are transient, disappearing quickly with the termination of the narcosis. Summated or cumulative effects are not observed. The irregularities which occur are varied, some closely resembling the effects produced by digitalis intoxication. G. H. S.

Relative absorption and the therapeutic efficiency of some bismuth preparations. L. G. BRINHAUER AND F. M. JACOB. *Am. J. Syphilis* 9, 213-24(1925).—As an anti-syphilitic agent Bi is as effective as regards the clinical manifestations of syphilis as is Hg, and is more effective in modifying persistent positive Wassermann reactions. All preps. of Bi are painless in administration, but with compds. which are quickly absorbed toxic effects are observed. With compds. which are absorbed slowly a cumulative effect must be considered. Therapeutic efficiency does not parallel absorption rate. G. H. S.

Clinical and biochemical study of neurosyphilis. IV. Relative distribution of arsenic in the liver, spleen, and kidneys of rabbits following the intravenous administration of silver arsphenamine. L. H. CORNWALL AND C. N. MYERS. *Am. J. Syphilis* 9, 256-61(1925); cf. C. A. 19, 680.—Detns. of As made on rabbits at intervals of from 1 to 98 hrs. after the intravenous injection of Ag arsphenamine showed larger quantities of the drug fixed in the spleen than in the liver or kidneys. After 4 days the amt. of As in the spleen was 12 times greater than that in the liver. G. H. S.

Tetrachloroethylene, a new anthelmintic. M. C. HALL AND J. E. SHILLINGER. *Am. J. Trop. Med.* 5, 229-37(1925).—As an anthelmintic  $\text{C}_2\text{Cl}_4$  is fully as effective as  $\text{CCl}_4$ , but apparently has no great advantages. G. H. S.

Elimination of bismuth in the urine in the treatment of syphilis with some ordinary preparations of bismuth. SVEND LOMHOLT. *Ann. dermatol. et syphil.* 6, 170-83(1925).—Water suspensions are absorbed much more rapidly than oil suspensions, the rate during the first 14 days being some 2 to 7 times greater. During the first 2 weeks an oil suspension of tartrobismuthate has an elimination rate almost double that of  $\text{C}_6\text{H}_5\text{N}_3\text{O}_2\text{BiH}_4$ , and this a rate almost twice that of  $\text{Bi}(\text{OH})_3$ . With sq. suspensions and solns. some 75% is absorbed within 14 days, the rates varying somewhat for different compds. G. H. S.

Reduction in the inflammatory response by administration of acid. KATE FUTER. *Arch. expil. Path. Pharm.* 105, 238-48(1925).—Repeated detns. in the same animal (rabbit) showed that the administration of HCl acts in the same way as  $\text{CaCl}_2$  in inhibiting inflammation. In both cases the acid-base equilibrium is shifted toward the acid side. With atophan the inhibitory effect is different, for here the  $\text{CO}_2$ -combining power of the blood is not disturbed. The effect is associated with a lowering of the temp. of the skin. G. H. S.

Percutaneous hormone therapy of rickets with "hormocutan." L. LANGSTEIN AND H. VOLLKER. *Z. Kinderheilk.* 39, 187-90(1925).—Detns. were made to ascertain if the marked reduction in the efficiency of pituitandol-salve, as compared with pure pituitandol, is due to the salicylic acid used in the prepn. of the salve. The results showed clearly that the acid, through contact with the hormone over a period of time, reduced, and later practically destroyed, the stimulating effect of the active substance upon metabolism. G. H. S.

Physiological action of phenolphthalein and allied substances upon the intestine. A. OGATA AND T. KONDO. *J. Pharm. Soc. Japan* No. 518, 339-51(1925).—In order to see what group in phenolphthalein is responsible for its action on the intestine, O. and K. compared the actions of the following allied compds.: 4,4'-dihydroxydiphenylmethane, 4,4'-dihydroxybenzophenone, 4'-hydroxydiphenylmethane-2-carboxylic acid, phenolphthalin, 4-(hydroxyphenyl)phenylphthalide, benzaurin, rosolic acid, phenolphthalol, dimethylanilinephthalin, and fluorescein. These compds. were dissolved in dil. alkali or alc. to make 0.1 M, and the effects of solvents detd. by controls. The results are given in 58 tracings. The action of phenolphthalein on the rabbit intestine is not necessarily due to the quinone group. Rather depends upon substitution on the diphenylmethane C atoms, that is, if 1 H of the methane is substituted by OH, and the other H by a large nucleus, as Ph, it increases the reaction. The absence of  $\text{CO}_2\text{H}$  group in phenolphthalein mol. rather increases its physiol. action, and the lactone ring is not necessary. S. T.

Experimental syphilis. III. Further observations on the possibility of cure of syphilis in the rabbit with arsphenamine. A. M. CHESNEY AND J. E. KEMP. *J.*

*Expt. Med.* 42, 17-31 (1923); cf. *C. A.* 18, 1715. Syphilitic rabbits can be treated with arsenamine in such a manner as to render the lymph nodes incapable of transmitting the infection to normal rabbits. This can be accomplished if treatment is begun early or comparatively late in the course of the disease. If treatment is begun early, the animals are almost uniformly susceptible to a second infection, whereas if it is begun late, they are almost uniformly refractory to a second infection. This refractory state in rabbits may be explained by the existence of an acquired immunity which persists after the abolition of the disease, rather than to the persistence of the first infection.

C. J. WUER

## 1 ZOOLOGY

R. A. GOETTER

Action of the principal metals in sea-water on the activation of eggs in course of hatching. DALCO. *Bull. hist. appl. physiol. path.* 1, 163-85 (1921). *Physiol. Abstracts* 9, 600.—Study of the influence of Ca, Mg, K, and Na ions on the parthogenesis of the eggs of *Asterias glacialis*. In this phenomenon, plasmolysis is independent of karyokinesis. The Ca ion accelerates the entrance to the egg during maturation. Na aids division of the cytoplasm, and Mg that of the nucleus. K appears to harmonize these 2 discordant actions. These are the 4 chief metals which induce maturation and parthogenesis.

H. G.

The measurement of the carbon dioxide output of fresh-water animals by means of indicators. J. T. SAUNDERS. *Proc. Camb. Phil. Soc. (Ecol.)* 1, 43-8 (1921). *Physiol. Abstracts* 9, 563.—A curve and tables are given relating the  $p_{\text{H}}$  of a dil. soln. of carbonates to its total  $\text{CO}_2$  content. Larvae of *Loimia vivipara* and eggs of *Rana temporaria* were placed in such dil. solns. and the change in  $p_{\text{H}}$  caused by their respiration was measured by the changing tint of cresol red. By this means an output of 0.0001 cc. per min. can be accurately estimated.

H. G.

The mode of transference of calcium from the shell of the hen egg to the embryo during incubation. G. D. HUCKNER, J. H. MARTIN AND A. M. PETER. *Am. J. Physiol.* 72, 253-6 (1923).—Expts. show that  $\text{H}_2\text{O}$  contg.  $\text{CO}_2$  when placed inside a carefully drained egg shell dissolves Ca from the shell as  $\text{Ca}(\text{HCO}_3)_2$ . In the incubating egg  $\text{H}_2\text{CO}_3$  produced by the embryo dissolves the Ca of the shell forming a sol., diffusible salt which is available for metabolism.

J. E. LYMAN

## 12—FOODS

W. D. UNDERLOW AND A. E. STEVENSON

Critique of modern food products and their methods of investigation. C. MARSCH. *Arch. Pharm.* 263, 302-75 (1923).—A lecture. See *C. A.* 19, 3002.

W. O. KERRY

The egg: Its composition and uses. ANON. *J. Dept. Agr. Union S. Africa* 10, 333-5 (1923).—The compn. and food value of eggs are summarized. Two samples of *nutrard powders* contained, resp., starch 86.23 and 26.35, albuminous compds. 11.89 and 2.90, coloring matter 0.88 and 0, hallog soda 0 and 50.70, tartaric acid 0 and 10.33,  $\text{H}_2\text{O}$  11.83 and 11.63%.

K. D. JACOB

A bibliography of researches bearing on the composition and nutritive value of corn and corn products. M. H. KRITH. *Illinois Agr. Expt. Sta., Bull.* 257, 151 pp. (1923).

J. J. SKINNER

Bacterial content of sweet corn. L. H. JAMES. *Canning Age* June 1923, 501-2.—A paper discussing the spoilage in sweet corn that occurs at the different stages of the canning process. These expts. made in a Middle-West canning factory during 1923 show very clearly the reasons why processing is attended with increased difficulties as a result of permitting the product to remain piled up overnight for any considerable length of time.

T. MARKOVITS

Role of acid in vegetable canning. W. V. CRESS AND W. V. FORD. *The Canner* 61, No. 2, 23-24 (1923).—The relation is given between H-ion concn. and sterilization, the changes in acidity during processing and the effect of acids on spoilage organisms.

T. MARKOVITS

Zinc in tinned and bottled peas. C. H. CRIMM AND A. J. STILL. *Analyst* 50, 296 (1923).—For fixing the green color, Zn salts are being used. To test, treat a sample as in the Kjeldahl method and to the clear soln. add  $\text{NaOH}$  till barely alk. and introduce  $\text{H}_2\text{S}$ . From this ppt. det. Zn as phosphate in the usual way.

W. T. H.

Electrocardiographic studies of the effects of ether upon the living cat's normal heart. H. R. MILLER, DAVID FELBERHAUM AND H. T. KRIGEL. *Am. J. Med. Sci.* 169, 516-31 (1925).—With adequate changes in the depth and duration of ether anesthesia cardiac abnormalities occur promptly but the irregularities are transient, disappearing quickly with the termination of the narcosis. Summated or cumulative effects are not observed. The irregularities which occur are varied, some closely resembling the effects produced by digitalis intoxication. G. H. S.

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Elimination of bismuth in the urine in the treatment of syphilis with some ordinary preparations of bismuth. SVEND LOMHOLT. *Ann. dermatol. et syphil.* 6, 170-83 (1925).—Water suspensions are absorbed much more rapidly than oil suspensions, the rate during the first 14 days being some 2 to 7 times greater. During the first 2 weeks an oil suspension of tartrobismuthate has an elimination rate almost double that of  $C_6H_5H_2N_3O_8-BiH_4$ , and this a rate almost twice that of  $Bi(OH)_3$ . With aq. suspensions and soins. some 75% is absorbed within 14 days, the rates varying somewhat for different compds. G. H. S.

Reduction in the inflammatory response by administration of acid. KATE FUERER. *Arch. expil. Path. Pharm.* 105, 238-48 (1925).—Repeated detns. in the same animal (rabbit) showed that the administration of HCl acts in the same way as  $CaCl_2$  in inhibiting inflammation. In both cases the acid base equil. is shifted toward the acid side. With atophan the inhibitory effect is different, for here the  $CO_2$ -combining power of the blood is not disturbed. The effect is associated with a lowering of the temp. of the skin. G. H. S.

Percutaneous hormone therapy of rickets with "hormocutan." L. LANGSTEIN AND H. VOLLMER. *Z. Kinderheilk.* 39, 187-90 (1925).—Detns. were made to ascertain if the marked reduction in the efficiency of pituitariol-salve, as compared with pure pituitariol, is due to the salicylic acid used in the prepn. of the salve. The results showed clearly that the acid, through contact with the hormone over a period of time, reduced, and later practically destroyed, the stimulating effect of the active substance upon metabolism. G. H. S.

Physiological action of phenolphthalein and allied substances upon the intestine. A. OGATA AND T. KONDO. *J. Pharm. Soc. Japan* No. 518, 339-51 (1925).—In order to see what group in phenolphthalein is responsible for its action on the intestine, O. and K. compared the actions of the following allied compds.: 4,4'-dihydroxydiphenylmethane, 4,4'-dihydroxybenzophenone, 4'-hydroxydiphenylmethane-2-carboxylic acid, phenolphthalin, 4-(hydroxyphenyl)phenylphthalide, benzauric, rosolic acid, phenolphthalol, dimethylanilinephthalin, and fluorescein. These compds. were dissolved in dil. alkali or alc. to make 0.1 M, and the effects of solvents detd. by controls. The results are given in 53 tracings. The action of phenolphthalein on the rabbit intestine is not necessarily due to the quinone group; rather depends upon substitution on the diphenylmethane C atoms, that is, if 1 H of the methane is substituted by OH, and the other 11 by a large nucleus, as Ph, it increases the reaction. The absence of  $CO_2H$  group in phenolphthalein mol. rather increases its physiol. action, and the lactone ring is not necessary. S. T.

Experimental syphilis. III. Further observations on the possibility of cure of syphilis in the rabbit with arsphenamine. A. M. CHESNEY AND J. E. KEMP. *J.*

*Exptl. Med.* 42, 17-31 (1925); cf. *C. A.* 18, 1715.—Syphilitic rabbits can be treated with arsphenamine in such a manner as to render the lymph nodes incapable of transmitting the infection to normal rabbits. This can be accomplished if treatment is begun early or comparatively late in the course of the disease. If treatment is begun early, the animals are almost uniformly susceptible to a second infection, whereas if it is begun late, they are almost uniformly refractory to a second infection. This refractory state in rabbits may be explained by the existence of an acquired immunity which persists after the abolition of the disease, rather than to the persistence of the first infection.

C. J. WEST

## I—ZOOLOGY

A. A. GORTNER

Action of the principal metals in sea-water on the activation of eggs in course of hatching. DALCO. *Bull. histol appl physiol. path.* 1, 465-85 (1924); *Physiol. Abstracts* 9, 600.—Study of the influence of Ca, Mg, K, and Na ions on the parthogenesis of the eggs of *Asterias glacialis*. In this phenomenon, plasmodieresis is independent of karyokinesis. The Ca ion accelerates the entrance to the egg during maturation. Na aids division of the cytoplasm, and Mg that of the nucleus. K appears to harmonize these 2 discordant actions. These are the 4 chief metals which induce maturation and parthogenesis.

H. G.

The measurement of the carbon dioxide output of fresh-water animals by means of indicators. J. T. SAUNDERS. *Proc. Camb. Phil. Soc. (Biol.)* 1, 43-8 (1924); *Physiol. Abstracts* 9, 585.—A curve and tables are given relating the  $p_H$  of a dil. soln. of carbonates to its total  $CO_2$  content. Larvae of *Zoarcetes viviparus* and eggs of *Rana temporaria* were placed in such dil. solns and the change in  $p_H$  caused by their respiration was measured by the changing tint of cresol red. By this means an output of 0.0001 cc. per min. can be accurately estd.

H. G.

The mode of transference of calcium from the shell of the hen egg to the embryo during incubation. G. D. BUCKNER, J. H. MARTIN AND A. M. PETER. *Am. J. Physiol.* 72, 253-5 (1925).—Expts. show that  $H_2O$  contg.  $CO_2$  when placed inside a carefully drained egg shell dissolves Ca from the shell as  $Ca(HCO_3)_2$ . In the incubating egg  $H_2CO_3$  produced by the embryo dissolves the Ca of the shell forming a sol., diffusible salt which is available for metabolism.

J. F. LYMAN

## 12—FOODS

W. D. BIGELOW AND A. E. STEVENSON

Critique of modern food products and their methods of investigation. C. MASATSCH. *Arch. Pharm.* 263, 362-75 (1925).—A lecture. See *C. A.* 19, 2092.

W. O. EMERY

The egg: Its composition and uses. ANON. *J. Dept. Agr. Union S. Africa* 10, 352-5 (1925).—The compn. and food value of eggs are summarized. Two samples of *custard powders* contained, resp., starch 86.25 and 26.38, albuminous compds. 0.59 and 2.96, sol. coloring matter 0.88 and 0, baking soda 0 and 50.70, tartaric acid 0 and 10.33,  $H_2O$  11.83 and 9.63%.

K. D. JACOB

A bibliography of researches bearing on the composition and nutritive value of corn and corn products. M. H. KEITH. *Illinois Agr. Expt. Sta., Bull.* 237, 151 pp. (1925).

J. J. SKINNER

Bacterial content of sweet corn. L. H. JAMES. *Canning Age* June 1925, 561-2.—A paper discussing the spoilage in sweet corn that occurs at the different stages of the canning process. These expts. made in a Middle-West canning factory during 1923 show very clearly the reasons why processing is attended with increased difficulties as a result of permitting the product to remain piled up overnight for any considerable length of time.

T. MARKOVITS

Role of acid in vegetable canning. W. V. CRUESS AND W. Y. FONG. *The Canner* 61, No. 2, 23-24 (1925).—The relation is given between H-ion concn. and sterilization, the changes in acidity during processing and the effect of acids on spoilage organisms.

T. MARKOVITS

Zinc in tinned and bottled peas. C. H. CRIBB AND A. L. STILL. *Analyst* 50, 286 (1925).—For fixing the green color, Zn salts are being used. To test, treat a sample as in the Kjeldahl method and to the clear soln. add NaOH till barely alk. and introduce  $H_2S$ . From this ppt. det. Zn as phosphate in the usual way.

W. T. H.

Tomato pulp—rapid determination of specific gravity. W. A. HUELSEN. *Canning Age* July 1925, 631-6.—The difficulty with most methods of detg the sp gr of tomato pulp is that they are not generally adapted to rapid use under factory conditions. H discusses the use of the refractometer for that purpose and tables are given showing the *N* and equiv sp gravities and total solids in tomato pulp. T MARKOVITS

Fermentation, processing and spicing of cucumber pickles. J. C. BELL. *Fruit Products J and Am Vinegar Ind* 4, No 10, 11-3, 23(1925).—A discussion of delivery of cucumbers, grading, location and size of tanks, salting, processing and formulas

J A KENNEDY

Composition of pure food preserves and jams. C. P. LATHROP. *Canning Age* July 1925, 625-8.—A discussion.

T. MARKOVITS

The proper application of pectin in jelly making. H. T. LEO. *The Canner* 61, No 2 41-3(1925).—L gives tables of the yield of jelly from varying amts. of sugar and pectin and the effect of inversion on b p of sirups

T. MARKOVITS

"Apple sugar" of Rouen. G A LEROY. *Ann fals* 18, 260-76(1925).—This is essentially a sort of "toffee" which originally was prepd. from sugar and apple juice; but at present it is generally prepd. without apples, and is flavored with lemon, though some confectioners still use a small proportion of apple juice. Pure samples prepd. in the lab showed d<sub>4</sub> (in spirits of turpentine) 1.520-1.530, sucrose 80.00-63.00, invert sugar 14.00-31.00, levulose 0.50-1.20, dextrin nil, total acidity (to litmus) trace, H<sub>2</sub>O and undetd. 5.50-4.80%. Com samples as manufd. at present always contain glucose and dextrins

A PAPINEAU COUTURE

The importance of dulcitol as a sugar substitute, from a hygienic standpoint. W A UGLOW. *Arch Hyg* 95, 89-100(1925).—Dulcitol possesses no bactericidal activity in the presence of saccharin. It kills small Crustacea in a diln of 0.02% and checks their reproduction in a diln of 0.007%. It has a retarding influence upon enzymes, a mild effect upon digestion by pepsin, a considerable effect upon the splitting of fat by the lipase of the pancreas and upon the amylolytic effect of diastase. It is destroyed by cooking with weak alkali (0.5-1.0%) and acid ( $1/4$ - $1/2$  N H<sub>2</sub>SO<sub>4</sub> or H<sub>3</sub>PO<sub>4</sub>). Decompn products (aminophenol) arise therefrom, which change oxyhemoglobin into methemoglobin. The poisonous activity of the dulcitol upon the blood is due to these decompn products. The same decompn products arise in the animal body and may be detected in the urine. A dose of about 0.1 g per kg. daily causes sickness. Therefore the use of dulcitol as a sugar substitute should be prohibited. F B SEINEAR

The problem of Noors honey. C. F. JURITZ. *J. Dept Agr. Union S Africa* 10, 334-7(1925).—Honey derived from several species of *Euphorbia*, and commonly known as "Noors honey," produces a strong burning sensation in the throat which may persist for several hrs. Analyses of specimens of the honey gave results which were within the limits for normal honey except for a slightly higher content in dry matter other than sugars. Ether extn gave a yellowish, waxy residue which was sepd into an impure wax and a non volatile, brownish oil that possessed the peculiar properties of the original honey. Alcoholic exts of *Euphorbia* flowers possessed similar characteristics. The active principle was not identified.

K. D. JACOB

The citric acid content of cow milk and its relation to the chlorine-sugar number as a criterion for normal and abnormal milk. F. KIEFERLE, J. SCHWABOLD AND CH. HACKMANN. *Z physiol Chem* 145, 18-36(1925).—By means of the micro-centrifugal method (CBr<sub>3</sub>COCHBr<sub>2</sub> method) the citric acid content of the milk from the 4 quarters of the udder was found to average 0.27%. Individual variations were observed with milk from the different quarters of the same udder and with different cows. The sep detns. come close to the av. value of 0.27, but in extreme cases vary from 0.40 to 0.12%. The relation between citric acid and lactose content cannot be recognized in av. samples from several milkings, but may be observed by comparing the milk from the different quarters of the same udder. Each quarter represents therefore a functional unit. The relation is such that a higher lactose content corresponds in general to a higher citric acid. Milk with an abnormally high Cl sugar no. generally shows a lower citric acid content.

A W. DOX

The effect of heat on the solubility of the calcium and phosphorus compounds in milk. R. W. BELL. *J. Biol. Chem.* 64, 391-400(1925).—By means of a Pasteur-Chamberland filter and a high-speed centrifuge, an attempt was made to det. the loss of soly of Ca and P in heated milk. After heating above 170° (F.) for 30 min. the effect was just perceptible and after heating to 212° (F.), the loss was less than 10% of the total sol. Ca or P present.

I GREENWALD

Causes of variation in cream tests. T. HAMILTON. *Rhodesia Agr. J.* 22, 48-58

(1925).—The details of handling, sepp and testing cream are discussed and improvements are suggested, which will tend to produce a product of uniform test. A. L. M.

Variations in the percentage of butter fat in milk. IV. Yearly variations. W. N. PATON *New Zealand J Agr* 30, 327-37(1925); cf *C A* 19, 2379.—Except for the factor of breed, yearly variations in the butter-fat content of milk due to the time of year of calving, length of period of gestation during test, condition of cow, feeding, etc., age of cow, and quantity of milk produced were found to be negligible. K. D. JACOB

New method for determining butter fat. G. VAN B. GILMORE. *Analyst* 50, 272-9(1925).—Introduce 5 g of fat and 7.5 g of glycerol into a small Erlenmeyer flask and add 2 cc of KOH soln (1:1). Heat carefully, with shaking, until a clear liquid is obtained. Add 20 cc of water and when the soap is all dissolved, transfer the soln to a 50 cc measuring flask. Make up to the mark and then transfer to a flask of about 175 cc capacity. Add 15 cc of 2/110  $N H_2SO_4$ . Shake about 1 min at 15-20° and filter, while keeping the fatty acid in the original flask. Transfer 50 cc of the filtrate to a 350-cc Erlenmeyer flask, add 100 cc of water and 0.1 g of powd pumice. Distil off 100 cc and titrate the acid in the distillate with 0.1  $N NaOH$ . The no. of cc. used can be called the *Gilman No.* of the fat. It is a measure of the butyric acid content. According to this method of analysis, butter gives a *Gilman No.* of 14-18, coconut fat 0.7-0.9, palm-kernel fat 0.4-0.6 and other, ordinary edible fats 0.1-0.2. The method is similar to that of Kirschner but is claimed to be superior. W. H. T.

Investigation of the constancy of the melting point and solidification point of butter fat. WALTER MOHR. *Milchwirtschaft Forsch* 2, 24-30(1924).—The influence of different factors such as the age, moisture, quantity of fat and temp. of cooling were investigated. The following method is recommended. The m. p. is detd. in a tube 1.8 cm. wide and contg. 15 cc. of fat, into which a thermometer, graduated in 0.1°, is placed. The fat is stirred and gradually warmed and the m. p. is obtained to within 0.3°. The solidification point is detd. in a 50-cc beaker, 4 cm. wide and contg. 35 cc. of fat at 50°. The beaker is placed in a const. temp. water bath (15°). The fat is rapidly stirred and the temp. is taken at 0.2° rise. The error is 0.2°. The m. p. and solidification point of butter fat are not absolutely definite points as in the case of pure compds. The butter must be filtered at 50-60°. No further drying is necessary. The age of the fat is without effect if the fat is preserved under  $CO_2$  in the cold. The fat, after being melted must be kept on ice 12-18 hrs. before the m. p. is detd. O. L. E.

Determination of fat in condensed milk. J. McCRAE. *Analyst* 50, 236(1925).—Dil. 40 g. of milk to 100 cc. Place 20 cc. in a Leffmann and Beam bottle, add 5 cc. of Fehling soln., shake and centrifuge. Shake the ppt. with water and again centrifuge. Repeat the washing a second time. Add 3 cc. of amyl alc. and 10 cc. of water to the ppt., which contains all of the fat. Add enough 90%  $H_2SO_4$  to bring the fat layer into the graduated part of the bottle. Warm, centrifuge and read at 65°. W. T. H.

The financial side of dairying. III. Balanced rations. E. W. SAMPSON. *J. Dept Agr. Union S. Africa* 10, 425-31(1925).—A table is given showing the percentages of dry matter, digestible flesh-forming material, and digestible fat-forming material in 13 green foods, 11 hays and straws and 12 concentrates used as dairy feeds in S. Africa. K. D. JACOB

The manufacture of Stilton and Wensleydale cheese. L. COLES. *J. Dept Agr. Union S. Africa* 10, 525-31(1925).—The manufacturing processes are outlined and discussed. K. D. JACOB

The ripening of cheese. F. W. J. BOEKHOUT. *Proc. World's Dairy Congress, Washington 1924*, 330-6; *Abstracts Bact* 8, 400.—The growth of lactic acid bacteria in milk is checked by the formation of acid in excess of the neutralizing power of the salts. In cheese, on account of the relatively high ratio of salts to lactose the acid is neutralized and the sugar is entirely fermented. The lactic bacteria cease growing because lactose, their principal source of C, is exhausted. They are followed by the rod-shaped bacteria which are able to convert the lactose into acid, but which continue to multiply after the sugar has disappeared. The lactic bacteria affect the ripening process in various ways. The endo-enzymes which are liberated when the dead cells disintegrate may be a factor. By increasing the acidity of the cheese they suppress the fermentative and putrefactive bacteria. The acid which they form produces conditions favorable for the action of the enzymes introduced with the rennet. Finally there is the chem. action of the acid on the Ca phosphates and the paracaseinates, which in some way not yet fully understood gives the requisite degree of softness to the curd. However, cheese made from milk drawn in an aseptic manner and inocu-

lated with the lactic bacteria is normal in appearance, but does not have the characteristic flavor. H. G.

The sunflower as a silage crop. W. B. NEVENS. Illinois Agr. Expt. Sta., Bull. 253, 185-225(1924).—The object of the work was to det. the stage of development at which the sunflower crop should be ensiled for the highest milk production. Sunflowers planted May 18 were cut August 13 when 23% of the plants were coming into bloom, on Sept. 1 when 95% of plants were in bloom and on Sept. 21 when plants had seed in dough stage. The earliest cutting was most palatable and contained more digestive nutrients and kept the milk flow at a higher level. Sunflower silage from mature plants was lower in dry matter, crude protein and N-free ext., but higher in crude fiber, ether ext. and ash than corn silage. The ensiling of the sunflower caused a small loss of crude protein and N-free ext. The org. acids were increased. J. J. S.

The preparation of acid feeds containing volatile fatty acids. L. Electrosilage of corn. C. BRAHM. Biochem. Z. 156, 15-20(1925).—Acetic, propionic, butyric, valeric, methylethylacetic and caproic acids were found to be present in the silage following acid fermentation of corn. F. A. CAJOZI

Buckwheat as a pig food. ANON. J. Dept. Agr. Union S. Africa 10, 372(1925).—The av. compos. of S. Africa buckwheat, buckwheat flour, buckwheat middlings, and maize pollard are given. K. D. JACOB

Determination of small amounts of Fe [in food products] (WALKER) 7. Tunnel apparatus for dehydrating fruits or vegetables (U. S. pat. 1,545,000) 1.

THOM, C. and HUNTER, A. C.: Hygienic Fundamentals of Food Handling. Baltimore: Williams & Wilkins Co. 228 pp. Reviewed in Expt. Sta. Record 52, 459(1925).

Coffee substitute. J. L. KELLOGG. U. S. 1,544,648, July 7. Sprouted grain, e. g., wheat and rye, is dried, inverted, again dried, and bran starches are converted into maltose by soaking bran in the inversion liquid from the grains. The grain and bran are then separately roasted and mixed. U. S. 1,544,649 specifies addn. also of a caramel liquid, before or after the roasting.

Apparatus for deodorizing cream by spraying and air treatment. O. F. HUNZIKER. U. S. 1,543,853, June 30.

Drying fruits, vegetables or other materials. H. D. BEAN and A. S. GLEN. U. S. 1,544,798, July 7. The material to be dried is subjected to the action of air under a pressure of about 100 lbs. per sq. in. in a closed container for a short time, the pressure is relieved and a blast of dry air applied for a short time.

Sterilizing peas or other foods in sealed packages. J. A. FENN. U. S. 1,544,304, June 30. A special method of utilizing superheated steam.

Canning and sterilizing fruits, vegetables, etc. W. B. FENN. U. S. 1,544,384, June 30. A special method of steam treatment.

Heat-treatment of canned foods. H. P. WELLMAN. U. S. 1,543,964, June 30. Mech. features.

Apparatus for dehydrating prunes, grapes, or other vegetable materials. C. C. MOORE. U. S. 1,543,947, June 30.

### 13—GENERAL INDUSTRIAL CHEMISTRY

HARLAN S. MINER

Chemical industry from the standpoint of national safety. GEORGES PATART. *Chimie et industrie* 13, 1021-30(1925).—An address. A. PAPINEAU-COUTURE

The relation of engineering education to industry. F. C. PRATT. *Gen. Elec. Rev.* 28, 468-71(1925). C. G. F.

The handwriting on the wall. A. D. LITTLE. *Ind. Eng. Chem.* 17, 857-8(1925).—The importance of research in various industries is discussed. E. H.

Usefulness of the chemical research laboratory in the oil and related industries. EMILE ANDRÉ. *Chimie et industrie* 13, 1031-7(1925).—An outline of its possibilities. A. PAPINEAU-COUTURE

Progress in the application of continuous hydrometallurgical methods in the chemical industry. J. V. N. DORE. *Trans. Am. Inst. Chem. Eng.* 16, Pt. 1, 185-201(1924).—A discussion of applications of, difficulties overcome by, and results obtained with the Dore methods and app. during the last 10 yrs. A. PAPINEAU-COUTURE

Theory of the vacuum drying processes. ARMAND MARTIN. *Chimie et industrie* 13, 883-9(1925).—Mathematical discussion. A. PAPINEAU-COUTURE

Some factors and principles involved in the separation and collection of dust, mist and fume from gases. EYALD ANDERSON. *Trans. Am. Inst. Chem. Eng.* 16, Pt. 1, 69-86(1924).—Brief outline of the nature of the dusts, fumes and mists and of the main methods used for their sepn. and collection, together with an analysis (largely mathematical) of the principles and factors involved in the different sepn. methods. A. PAPINEAU-COUTURE

The inorganic dust of respiratory air in industrial trades and its gravimetric estimation. V. FROBOESE. *Arch. Hyg.* 95, 174-87(1925); *Arch. Reichsgesundheitsamte* 55, 593-606.—A filtering app. is described and pictured and a method of weighing the filtered dust is given. A discussion and tabulation of the amt. of dust in the air in cast-iron dressing and casting industries, etc., are given. F. B. SEIBERT

Lime dermatitis. W. J. O. DONOVAN. *Lancet* 1925, I, 599-602.—Lime dermatitis may be encountered in a wide field of industrial life. The types of dermatitis, the predisposing causes and preventive measures are given. F. B. SEIBERT

BINZ, ARTHUR: *Chemische Technologie*. Berlin: J. Springer, 81 pp. R M 3.90. Engineers and Chemists. Status and Employment in Industry. Studies and reports, Series L. (Professional Workers) No. 1. International Labor Office. Geneva, Switzerland. Boston, Mass. 40 Mt. Vernon St.: World Peace Foundation. Price 30 cents. Reviewed in *Ind. Eng. Chem.* 17, 875(1925).

Concentrating solutions. N. C. CHRISTENSEN. U. S. 1,544,130, June 30. A revolving drum touches the surface of a body of a salt soln. or other soln. to be evapod. and throws a spray from its periphery to facilitate evapn.

Separating gaseous mixtures. SILICA GEL CORPORATION. Brit. 227,309, March 11, 1924. In removal of moisture from air or other gases, recovery of SO<sub>2</sub>, ether, acetone, C<sub>2</sub>H<sub>6</sub>, gasoline, etc., from mixts. with air or other gases, an adsorbent material such as silica gel, activated C. or gels of Sn, W, Al, Th and Fe is injected into the gas stream and carried along with it; it is afterward sepd. and reactivated. An app. is described.

Storing dissolved gases. E. E. PETITPIERRE. U. S. 1,543,679, June 30. Peat in compressed elastic form is used as a filling in storage vessels such as those for holding C<sub>2</sub>H<sub>6</sub>, dissolved in acetone.

Rectifying and heat-interchange system for separating xenon, krypton, etc., by liquefaction, etc. Soc. L'AIR LIQUIDE, Soc. ANON. POUR L'ÉTUDE ET L'EXPLOITATION DES PROCÉDÉS G. CLAUDE. Brit. 227,800, Jan. 19, 1924.

Heat-insulation. C. S. TEITSWORTH. U. S. 1,544,196, June 30. A compn adapted for insulating steam pipes, etc., comprises diatomaceous earth, port. cement or other binder, a gelatinous gum such as gum karaya and asbestos or other fibrous material.

Connecting insulator parts. M. F. H. GOUVERNEUR. U. S. 1,544,148, June 30. Powd. Cu or other metallic powder is applied to surfaces of insulator parts or similar materials to be connected and they are then joined with the aid of an interposed layer of granulated porcelain or other granular material which is also coated with the metal powder. Cf. C. A. 18, 2776.

Heat-insulation. L. CALDWELL. U. S. 1,544,215, June 30. Diatomaceous earth or other inorg. heat-insulating material is mixed with gum karaya, H<sub>2</sub>O and Na<sub>2</sub>CO<sub>3</sub> and heated.

Refrigerating system. E. B. MILLER and A. BENZON. Brit. 228,136, Jan. 23, 1924. Vapor from a brine or H<sub>2</sub>O evaporator is adsorbed by silica gel, activated charcoal or similar material. Various details are specified and an app. is described.

## 14—WATER, SEWAGE AND SANITATION

EDWARD BARTOW AND G. C. BAKER

Colloids and mineral waters. D'ARSONVAL and BORDAS. *Compt. rend.* 179, 912-3(1924); cf. C. A. 19, 689.—Certain mineral waters deposit sediment after being bottled. The deposition of sediment may be avoided by adding CO<sub>2</sub> to avoid both oxidation and pptn. from acid carbonates. Certain cases of deposition, however, do not seem to be traceable to these 2 causes. B. C. A.

Chemical character of ground waters of the northern Great Plains. H. B. RIPPEN-

BURG U. S. Geol. Survey, *Water-Supply Paper* 560B, 31-52(1925).—The waters of the Dakotas and Montana to the foothills of the Rocky Mts. are included in this study, which is based on more than 1000 analyses. The ground waters are in general of meteoric origin and have replaced the waters of sedimentation as shown by their small Cl content. Tilting of strata, cementation, heat and chem. and mineral changes within the rocks have assisted in the migration and expulsion of the interstitial waters. The changes in meteoric waters, from the time they entered the soil to the time they were analyzed, have resulted from the soln. of Na, Ca and Mg carbonates and sulfates, from redeposition and exchange on the part of the constituents, and from chem. reactions brought about by the oxidation of pyrite or by the reduction of sulfates. L. W. RIGGS.

Coastal ground water with special reference to Connecticut. J. S. BAOWN. U. S. Geol. Survey, *Water-Supply Paper* 537, 97 pp (1925).—A study of shallow wells along the Conn. coast near New Haven was made with particular reference to the conditions affecting contamination by sea water. More than 180 sources were examd. in which the amt. of Cl served as an indicator of the presence of salt water. An extensive bibliography of coastal ground waters is given. L. W. RIGGS.

Temperature of water available for industrial use in the U. S. W. D. COLLINS. U. S. Geol. Survey, *Water-Supply Paper* 520F, 97-104(1925).—The temp. of ground water is generally 2 to 3° F. above the mean annual air temp. if the water is 30 to 60 ft. below the surface of the ground. At a depth of 10 ft. the range may be 10° F. above or below the mean annual temp. The mean monthly temp. of a surface water is generally within a few degrees of the mean monthly air temp. if it is above the f. p. L. W. RIGGS.

Recommended specification for quicklime and hydrated lime for use in the purification of water. ANON. Bur. Standards, *Circ.* No. 231, 4 pp.(1925). E. H.

Huntington, W. Va., water facilities have interesting features. ANON. *Ry. Eng. & Maintenance* 21, 263(1925).—The C. and O. R. R. has recently installed the largest intermittent water-softening plant in Railway Service at Huntington, W. Va. Water is used from the Guyan River, which is badly polluted at times by acid drainage from coal mines. Lime and  $\text{Na}_2\text{CO}_3$  are used in 2 steel tanks, and the water is treated in batches of 500,000 gal. Floating suctioners are provided in the tanks to automatic transfer pumps to the distribution system. Capacity is estd. at 3 M. G. D.  $\text{Na}_2\text{AlO}_2$  is being used to aid clarification. Detail piping diagram and photographs are shown. R. C. BARWELL.

New water facilities at Russell, Ky., insure adequate supply. ANON. *Ry. Eng. & Maintenance* 21, 191(1925).—The C. and O. R. R. recently completed improvements to their water supply facilities at Russell, Ky., which included an 80,000-gal.-per-hr. continuous lime and soda ash water softening plant to remove the sand and acid scale from the Ohio R. water for use in locomotives.  $\text{Na}_2\text{AlO}_2$  is used to aid clarification. Description, plans and photographs of pumping machinery as well as softening equipment are given. R. C. BARWELL.

Electrolytic conductivity and hydrogen-ion control of waste disposal. H. C. PARKER. *Trans. Am. Inst. Chem. Eng.* (advance copy) June 1925, 3-18.—Recent improvements in cells and electrodes appear to make their use in waste control feasible. Recording and controlling instruments are available to meet any given set of conditions. This control is the only method which accommodates variations in (1) the concn. of applied chemicals, (2) the flow of the influent, (3) the concn. of the influent. Records are given of automatic control in the direct oxidation of sewage at Allentown, Pa. H. C. PARKER.

Boiler-feed-water purification. EMILE HUC. *Papier* 28, 407-9(1925).—Brief discussion of the various methods of purification, and more particularly of the merits of the continuous blow-down method. A. PAPINEAU-COUTURE.

Concentration in boilers. G. D. BRADSHAW. *Proc. Eng. Soc. Western Pennsylvania* 41, 105-32(1925).—The concn. which causes foaming depends upon the salt concn. of the water, the soltness of the water, the concn. of the oil, vegetable matter, etc., and upon the design of the boiler. Concn. will vary directly with the quality of the feedwater and inversely with the % of water blown out of the boiler. A balance is always established between the impurities entering the boiler with the feed water and the sum of the impurities leaving in the steam. When concns. have been measured a check upon them should be obtained by working up a "dirt balance." Discussion brought out that  $\text{BaCO}_3$  treatment has resulted in large overall savings and reduced the boiler concn. about 94% max. The effects on concn. brought about by "zeolite," lime and soda ash, and lime and  $\text{BaCO}_3$  treatments are shown in a chart. W. H. B.

Filtration of water with membrane filters. R ZSIGMONDY. *Z. Hyg.* 102, 97-108 (1924). —The technic is given of producing potable  $H_2O$  on a small scale from contaminated sources by means of membrane filters (cf. Zsigmondy and Bachmann, *C. A.* 12, 2262). The slimy material in some waters that clogs the pores of the filter can be removed with  $FeCl_3$  and  $CaCO_3$ . The filters can be cleaned by scouring with emery, carborundum or quartz.

JULIAN H. LEWIS

Economical use of alum in mechanical filters. A D STEWART AND RAO SAHIB V. GOVINDA RAJU *Indian J Med Research* 12, 731-4 (1925). —"Rapid sand filters, when waters are filtered that are not turbid but have had some sort of storage, reach their max. filtering efficiency after being fed with coagulated water for an hr. only." The use of alum thereafter can be dispensed with.

FRANCIS KRASNOW

The investigation of ventilation. ROBERT C FREDERICK. *Analyst* 50, 213-24 (1925). —An interesting discussion of the factors involved in ventilation and description of simple methods for detg  $CO_2$  content, temp and humidity, cooling power, and air movement.

W T. H

Purification of tannery sewage (THIAU, FAVRE) 29. The corrosion problem in connection with water-works engineering (SPELLER) 9. Action of natural waters on Cu (HENSTOCK) 9. Electric purification of water (U. S. pat 1,544,052) 4. Carbonizing coal, etc. (sewage) (Brit. pat 227,890) 21.

Softening water. F. SCHMIDT. Brit. 227,429, Jan 12, 1924.  $H_2O$  is treated with a mixt. of caustic alkalis, alkali carbonates and borates, and alkali salts of acids insol. in  $H_2O$  such as silicates, aluminates and aluminosilicates. Clay, casein or mucilaginous substances may be used in prepg the compns. in pasty or solid form. The sediment from the treated  $H_2O$  may be used as a scouring powder.

Glauconite for water-softening. C. H. NORDELL. Brit. 227,785, Jan 17, 1924. See U. S. 1,506,198 (*C. A.* 18, 3244).

Apparatus for softening water with zeolitic material, etc. J. BRANDWOOD. Brit. 227,707, May 22, 1924.

Apparatus for purifying water by heating. E. F. RORKE. U. S. 1,544,348, June 30. Filter bed for treating water. F. P. CANDY. Brit. 227,258, Dec. 1, 1923. A float-controlled valve governs discharge of  $H_2O$  from the filter.

Base-exchanging silicates. V. KOBELT. Brit. 227,631, Jan 23, 1924. Substances such as clay which has been burnt at 500-700° or yellow brick, which have low base-exchanging properties, are improved in this respect by treatment with  $HCl$  in dil. soln., followed by washing until neutral, with or without an additional treatment with boiling alkali soln. or an ammoniacal soln. of  $CaCl_2$ . The product is suitable for use in purifying  $H_2O$  and it may be regenerated with  $NaCl$  soln.

Sewage treatment. H. DORFMÜLLER. Brit. 227,676, April 4, 1924. Sewage is passed continuously through a settling chamber in which floating and heavy substances sep. and pass through apertures at the top and bottom into a chamber where they are subjected to anaerobic decompn.

Sewage treatment. A. MACLACHLAN. U. S. 1,543,939, June 30. Sludge is sep'd. from sewage and sterilized. The solid contents of the sludge are then gathered upon a sheet-forming screen, the sheet is removed from the screen and  $H_2O$  is squeezed from it.

## 15—SOILS, FERTILIZERS AND AGRICULTURAL POISONS

J. J. SKINNER

The Woburn experimental farm and its work (1876-1921). J. A. VOELCKER. *J. Roy. Agr. Soc.* 84, 110-66 (1923). —A review of the expts. carried out and the conclusions reached at this farm during its 46 yrs. of existence. The expts. include, growing the same crops on the same plots annually for 45 yrs., applying the same fertilizers to the same soil annually for very long periods, comparison of the effect of various fertilizers on different crops, sugar content of beets, liming tests, stock-feeding, ensilage, green-manuring, and the effect of a great variety of chemicals upon wheat, in addn. to others of lesser interest to chemists.

A. L. MEHRING

Research work by the Society in 1923. Experiments with cereals in Norfolk. C. HEIGHAM. *J. Roy. Agr. Soc.* 84, 166-73 (1923). —None of the fertilizers applied increased the crop yields materially, and this is believed to be due to drought during most of the growing season.

A. L. MEHRING

Annual report of the agricultural chemist to government, Punjab, for the year ending 30th June, 1923. P. E. LAKBER. *Report Operations Dept. Agr., Punjab*, 1922-3, Part 2, 73-123(1924).—Higher yields of cane, juice and gur were obtained from plots of sugar cane treated with gypsum than from control plots ( $\text{NH}_4)_2\text{SO}_4$  applied alone at the rate of 300 lbs. per acre, gave a higher content of juice and sucrose in sugar cane than the same amt. of  $(\text{NH}_4)_2\text{SO}_4$  applied in a complete fertilizer. Tables are given showing the juice, sucrose and invert sugar content of different varieties of sugar cane at various stages of growth. Treatment with gypsum did not have an appreciable effect upon the amt. of  $\text{H}_2\text{O}$ -sol matter in Bara soils. *Fermentation of wheat dust*—A sample of wheat dust contained org. N 1.33,  $\text{K}_2\text{O}$  0.53, and  $\text{P}_2\text{O}_5$  0.73%. Portions of this material were inoculated with farmyard manure and with soil and allowed to ferment. The protein content dropped from 16 to 1.03% in 7 weeks, remaining const thereafter, and the  $\text{NH}_4$  content increased correspondingly. In pot expts the fermented dust gave results comparable with those obtained from farmyard manure. *Road earths*—Mech. and chem. analyses are given of 32 samples of soils from roads. No correlation existed between the compn. of the soils and their value for road building. *Detection of small quantities of phosphates*.—An increase in the  $\text{P}_2\text{O}_5$  content of soils could not be detected by the usual volumetric and gravimetric methods when superphosphate was applied in amts. less than 700 lbs. per acre. With larger amts, the added  $\text{P}_2\text{O}_5$  could be detected but could not be estd. accurately. *Soil surveys*—Mech. and chem. analyses of soils and well waters from the area covered by the Jalalpur canal project are tabulated. *Bacteriological*.—The presence of protozoa increased the fixation of N by soil bacteria by as much as 48%. Solid media were superior to liquid media for the growth of protozoa and better growth was obtained in media of higher concns. than those ordinarily used for bacteria cultures. Ciliates and amoebae grew well in media of  $\text{pH}$  3.7 to 9.75, and flagellates in media of  $\text{pH}$  4.5 to 9.75.

K. D. JACOB

Theory of adsorption and soil gels. N. E. GORDON. *2nd Colloid Symposium* 1925, 114-25; cf. *C. A.* 18, 608.—A colloid gel of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  lies between the silicate particle and the film of adsorbed water. This intermediate film holds salts in its interstices so that they cannot be speedily leached out, e. g., by a heavy rain, although plant expts. show them to be available as plant food. Adsorption of metals by  $\text{SiO}_2$  hydrogels led to the view that a certain no. of the surface mols. of the  $\text{SiO}_2$  ultramicros are ionized; this explains the charge on the  $\text{SiO}_2$  gel, which is negative until the  $\text{pH}$  is 1.217 or over, when it becomes positive. Peptization occurs at about  $\text{pH}$  7. The fixation of the metal hydroxide by adsorption also accounts for some of the soil acidity. Both acids and bases release K from adsorption by  $\text{SiO}_2$ . Dyes cannot be used to ascertain the colloidal content of soils.

JEROME ALEXANDER

The role of colloids in soil moisture. GEO. J. BOUYOUCOS. *2nd Colloid Symposium* 1925, pp. 126-34.—A discussion of the attraction of soils for water, heat of wetting (from which colloid content of soil may be estd.), wilting coeff. (water left in a soil when the exptl. plant wilts),  $\text{L}$  p. depression, and unfree water (which will not freeze out), moisture-holding capacity, permeability and capillary rise. Much of the information is qual. in nature, and quant. investigations are needed.

J. A.

Saturation capacity of mineral soils. D. J. HIRSCH. *Z. Pflanzenernähr. Düngung* 4A, 137-58(1925).—Methods for detg. the degree of satn. and the satn. capacity of soils are described. The bearing of such values upon the  $\text{pH}$  value, the CaO requirement and the state of flocculation of the colloids is discussed. When the Ca is represented as a percentage of the clay present, a high degree of correlation exists between the satn. values and the replaceable Ca present. Equiv. wts. of humus and of clay give conductometric values of about 18 and 115, resp.

A. L. MEHRING

Determination of the acidity of mineral soils. G. HAGER. *Z. Pflanzenernähr. Düngung* 4A, 159-77(1925).—Various methods for detg. CaO requirements are discussed.

A. L. MEHRING

The presence of nitrates in forest soils. A. NEMEC AND K. KVAPIL. *Compt. rend.* 180, 1431-3(1925).—A table is presented of detns. of nitrate in the dead layer, humus, vegetative soil and mineral soil under various types of forest vegetation. The nitrate content of the humus of pine appears to decrease as the age of the growth increases. The humus and dead layers under broad-leaved growth are relatively rich in nitrate; in particular the dead layer under copses of young ash showed a very high content. All the layers under a mixed growth of pine and beech were much richer in nitrate than those of pure stands of pine in the same region.

P. R. DAWSON

The carbon dioxide of arable soil—green coal. REINAC. *Z. Ver. deut. Ing.* 69, 717-22(1925).—Data are cited (cf. *C. A.* 19, 2359) showing that the soil is the source

of a large share of the  $\text{CO}_2$  utilized by plants. The C of the soil and its release through various decompn. processes is discussed. Various economic aspects of this C distribution are considered. P. R. DAWSON

The availability of phosphorus in calcareous and non-calcareous soils. J. W. AMES AND C. J. SCHOLLENBERGER. Ohio Agr. Expt. Sta., Bull. 380, 215-42(1924).—Fertilization expts were conducted on several soil types to test the effect of lime upon the availability of P. As a rule lime had very little effect either upon the availability of the native P supply or upon added P. This was shown both by the crop yield and by the P content of the grain. With wheat, the P content of the grain was in several instances increased by the lime treatment. Analyses of oat plants showed that the differences in P content attributable to fertilization become less as age of the plant increases. After 8 years in cylinders, the most pronounced changes in compn. of the soils were in Ca sol. in dil. acid and in reaction. The soils became much more acid. In some cases there was appreciable decrease in sol. P. In every case org. P was higher in unlimed soil than in original soil. M. S. ANDERSON

The gravimetric determination of phosphoric acid. W. H. ROSS, R. M. JONES AND A. R. MERZ. J. Assoc. Official Agr. Chemists 8, 407-9(1925).—Four different phosphate materials were analyzed by the same gravimetric procedure with the variation that in one set of expts. the solns. were made exactly neutral before adding the magnesia mixt., in another set they were made alk. by the addn. beyond the neutral point of 1 cc. of 0.90 sp. gr.  $\text{NH}_3$ , and in a third set they were made acid by the addn. of 1 cc. of 1.18 sp. gr.  $\text{HCl}$ . The results showed that highest values were obtained with the acid solns. and lowest with the alk. solns., but the differences were so slight as to be almost within the limit of expl. error. W. H. ROSS

Acid phosphate and soil acidity. C. A. WHITTLE. *Citrus Ind.* 4, 32(1923); *Botan. Abstracts* 14, 142.—Long use of acid phosphate by various expt. stations is said to show no sign of increased soil acidity, and agricultural authorities are said to agree that acid phosphate causes no injury. H. G.

Significance of the kind of soil acidity for the solution of sparingly soluble phosphates. H. KAPPEN AND K. BOLLENBECK. *Z. Pflanzenernähr. Düngung* 4A, 1-29 (1925).—A soln. of humic acid dissolves  $\text{Ca}_3(\text{PO}_4)_2$ . More phosphate is dissolved in a soil of the same pg value when the acidity is due to neutral salt decompn. than when due to hydrolytic dissociation and less when due to base exchange. The presence of  $\text{K}_2\text{SO}_4$  or colloidal  $\text{SiO}_2$  increases the soly. in each case, but artificial permutites do not. A. L. MEHRING

Effect of silicic acid on the morphological and anatomical structure of rye straw with a deficiency of phosphate. H. WIESSMANN. *Z. Pflanzenernähr. Düngung* 4A, 73-83(1925).—Colloidal  $\text{SiO}_2$  increased yields of rye grown in nutrient solns. lacking in  $\text{P}_2\text{O}_5$ . The  $\text{SiO}_2$  content of the straw was greatly increased but that of the grain only slightly. The anatomical structure was the same in each case but there were more nodes on the  $\text{SiO}_2$ -treated straw. A. L. MEHRING

Conversion of calcium oxide into calcium carbonate in the soil and the cause of its combination. E. BLANCE AND F. SCHEFFER. *Z. Pflanzenernähr. Düngung* 4B, 66-9 (1925).—The belief that  $\text{CaO}$  is quantitatively converted into  $\text{CaCO}_3$  in the soil is found to be incorrect. The amt. of  $\text{CO}_2$  combining with  $\text{CaO}$  never exceeded 80% of that required for satn. in any of the expts. but it varied with the type of soil used. The presence of Na, K or Ca permutites or previous extn. with  $\text{HCl}$  did not affect the rate of formation of  $\text{CaCO}_3$ .  $\text{SiO}_2$  gel decreased the amt. of carbonate formed, but  $\text{Al}_2\text{O}_3$  gel did not. It is believed therefore that some of the  $\text{CaO}$  combines with  $\text{SiO}_2$  in the soil to form silicates. A. L. MEHRING

Some properties of urea in relation to soil. P. COUTURIER AND S. PEKRAUD. *Compt. rend.* 180, 1433-6(1925); cf. C. A. 19, 1025.—No absorption of urea from soln. could be detected in the case of soils first treated with water contg.  $\text{CHCl}_3$ . Apparent retention when the soil is not thus treated is due to the rapid conversion by bacterial action of the urea into  $(\text{NH}_4)_2\text{CO}_3$  and the absorption of the latter; this prevents undue losses through leaching. The conversion of urea into  $(\text{NH}_4)_2\text{CO}_3$  takes place so rapidly that at  $17^\circ$  it is practically complete after 24 hrs., while at  $2^\circ$  it is complete within 5 days. P. R. DAWSON

Soil water of the New Jersey coast. A. P. KELLY. *Ecology* 6, 143-9(1925).—Tabulated results are presented of 113 tests made on the sea beach of the northern New Jersey Coast. In confirmation of previous work, it was found that the sea beach is saline only under the influence of the surf and that fresh soil water may be found even under the dunes. While the ground water of the front beach is alk., it quickly becomes acid on the landward side, changing rather rapidly upon coming into a region

presenting a different physico-chem complex; the local reaction is caused largely by local conditions. In dune soils the reaction curve proceeds steadily from acid to less acid (just as in sandy soils of the interior), whereas these soils, where humus is present in appreciable amt., exhibit the depressed curve of most inland soils. P. R. DAWSON

Influence of humic acids on the bacterial life of moorland soils and methods of determining soil acidity. T. ARND. *Z. Pflanzenernähr. Düngung* 4A, 53-72(1925).—Ammonification and denitrification were most active when sufficient CaO was added to acid soils to neutralize them. Nitrification took place only on the alk. side of neutrality. The Tacke Suchting method for CaO requirement is satisfactory. Gally's method gives higher and Daikuhara's method lower figures. A. L. MEHRING

The use of gypsum for soil improvement. A. A. RAMSAY AND A. N. SHEPHERD. *J. Agr. Gaz. N. S. Wales* 36, 259-63(1925).—Samples of gypsum from the Doliddy Swamp deposits contained  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  61.8-76.5%. Samples from the Trida-Ivanhoe deposits contained  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  79.40-98.38,  $\text{CaCO}_3$  0-8.57, and gang 1.62-17.32%. Applications of gypsum greatly increased the  $\text{H}_2\text{O}$ -absorptive powers of red clay soils. K. D. JACOB

Lime requirement of soils from the standpoint of plant physiology. II. Soil reaction and the growth of the higher plants. O. ARRHENIUS. *Z. Pflanzenernähr. Düngung* 4A, 30-52(1925), cf. C. A. 19, 1749.—Curves representing the growth of various plants in soil of varying acidity show 2 maxima. These vary in position with the species. The compn. of the ash and crop yields varied with the acidity. A bibliography is appended. A. L. MEHRING

Problems of liming soils. A. GEHRING. *Z. Pflanzenernähr. Düngung* 4B, 70-7(1925).—The addn. of  $\text{Ca(OH)}_2$  or  $\text{CaCO}_3$  to soils increased the rate of percolation of  $\text{H}_2\text{O}$  through some and diminished it through others. These expts. may indicate why liming some acid soils does more harm than good. A. L. MEHRING

Liming materials. W. H. SHAW. *J. Assoc. Official Agr. Chemists* 8, 344-53(1925).—A collaborative comparison was made of the modified Scaife, the modified Proctor and the modified Stone and Scheuch methods for detg. CaO and  $\text{Ca(OH)}_2$  in burnt and hydrated limes. The Scaife method proved to be the most accurate and the Stone and Scheuch method the least, but satisfactory results were obtained with the last-mentioned method when further modifications were applied by S. It is recommended that the Proctor method be deleted as a tentative method of the A. O. A. C. and that the other 2 methods be continued for further study. W. H. ROSS

Persistence of dicyanodiamide nitrogen in a molded calcium cyanamide after some months in the soil. A. ACCUET AND A. BRUNO. *Compt. rend.* 180, 1436-8(1925).—Two samples of  $\text{CaCN}_2$  molded in little sticks contain, after several months in the soil, 1.26 and 0.91% N, resp., all of which was shown to be dicyanodiamide. A fresh sample of a product of the same manuf. contained 7.15% dicyanodiamide N with 7.77% cyanamide N. The necessity for care to avoid such concns. of dicyanodiamide in the manuf. of such products is emphasized. P. R. DAWSON

Methods of determining the fertilizer requirement of soils. I. GERLACH. *Z. Pflanzenernähr. Düngung* 4B, 25-31(1925).—Mitscherlich's formula for the detn. of the fertilizer requirement of soils is criticized. It is claimed that the results obtained with his constant do not agree with those obtained in field tests. II. H. NEUBAUER. *Ibid.* 32-4.—Figures are presented showing good agreement between the  $\text{P}_2\text{O}_5$  requirement as detd. by his method (cf. C. A. 18, 877) and pot culture expts. with the same soil. III. H. NIKLAS. *Ibid.* 35-6.—The  $\text{P}_2\text{O}_5$  requirement of soil may be detd. by the rate of growth of *Atolobacter* in it under certain conditions. The results are in good agreement with those obtained by Neubauer's and Lemmermann's methods. IV. O. LEMMERMAN. *Ibid.* 37-41.—Detn. of the  $\text{P}_2\text{O}_5$  requirement by the ratio of citric acid-sol. to total  $\text{P}_2\text{O}_5$  gave results in good agreement with Neubauer's method and both methods agreed with field tests in 75% of the trials. No method equals a field trial. A. L. MEHRING

Soil potassium as affected by fertilizer treatment and cropping. J. W. AMES AND R. H. SIMON. *Ohio Agr. Expt. Sta., Bull.* 379, 185-212(1924).—Water and 0.01 N acid extns. made of soils from fertility exptl. plots show that the supply of active K in silt loam soil has been gradually depleted where large yields have been produced by addns. of lime and acid phosphate. Soils fertilized with  $\text{NaNO}_3$  contained slightly increased amts. of  $\text{H}_2\text{O}$ -sol. K. Soil to which KCl was applied contained an increased amt. of K in the subsoil. K applied in stable manure was not carried in the subsoil as was K applied as KCl. There was a decrease in 10 yrs. of active K on unfertilized soil where potatoes were grown.  $\text{CaSO}_4$ ,  $\text{NaNO}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$  and monocalcium phos-

phate in 2% solns increased the sol of K in silt loam, clay loam and clay soils, which were unfertilized and fertilized with K. J. J. SKINNER

Importation of fertilizers in 1924-25. F. T. LEIGHTON. *New Zealand J. Agr.* 30, 318-9(1925)—Statistical. K. D. JACOB

Statistical study of the fertilizer experiments of the Lauchstadt and Gross-Jübars experiment farms. W. SCHNEIDEWIND. *Z. Pflanzenernähr. Dungung* 3B, 313-25 (1924)—In all expts in which the same fertilizer was applied to the same soil over a long period of years the yields did not diminish whether manure or com. fertilizer was used. The absence of either  $K_2O$ ,  $P_2O_5$  or N was much more severely felt on plots receiving com. materials contg equiv amts of plant food than on those receiving manure.

The availability of organic nitrogenous fertilizers. W. C. DELONG. *Sci. Agr.* 5, 205-10(1925)—A résumé. P. R. DAWSON

The determination of available nitrogen in mixed fertilizers by the official neutral permanganate method as used in Florida. G. HARR. *J. Assoc. Official Agr. Chemists* 8, 417-9(1925)—Remarks on the application of the method in meeting the requirements of the Florida law. P. R. DAWSON

Fertilizer experiments combined with different soil cultivations in 1923. F. GLANZ. *Z. Pflanzenernähr. Dungung* 3B, 283-300(1924)—The effects of different systems of cultivation of oats on the fertility of the soil and the colloids in it are discussed. A. L. MEHRING

Influence of phosphate fertilizing on the vitamin B production in plants. C. HORNE-MANN. *Z. Pflanzenernähr. Dungung* 4A, 84-104(1925)— $P_2O_5$  did not increase the vitamin B content but did increase the crop yield in all cases. A. L. MEHRING

Toxicity studies with dicyanodiamide on plants. F. E. ALLISON, J. J. SKINNER AND F. R. REID. *J. Agr. Research* 30, 419-29(1925)—Results obtained in pot expts. with wheat using 2 kinds of soil indicate that dicyanodiamide is not a marked direct poison for this crop but is merely unavailable as a plant food and probably prevents the proper utilization of the soil N. The injury to wheat was slight even at the high concn. of 40 lb of  $NH_3$  equiv. per acre and the addn. of 5-10 lb. of  $NH_3$  as  $NaNO_3$  was sufficient to counteract any decrease in wt. caused by this concn. of dicyanodiamide. Expts. with cowpeas showed that this plant is injured by applications of dicyanodiamide contg as low as the equiv of 5 lb of  $NH_3$  per acre.  $NaNO_3$  did not counteract the injury and even increased it in several instances. Conclusion Dicyanodiamide may be very toxic to some plants and nearly inert to others. W. H. ROSS

Preliminary note on the stimula treatment of seeds. ANON. *J. Dept. Agr. Union S. Africa* 10, 299(1925)—Specimens of seed-maize were soaked for 12 hrs. prior to drying and planting, in 3% solns of  $MgCl_2$ ,  $Ca(NO_3)_2$ ,  $NH_4NO_3$ ,  $(NH_4)_2SO_4$ ,  $NaNO_3$  and  $NH_4$  phosphate. In general the highest percentages of germination were obtained from the untreated seed and the lowest from seed treated with  $NH_4NO_3$ . Seed treated with  $(NH_4)_2SO_4$  solns gave the highest yields of ensilage and the untreated seed gave the lowest yields. K. D. JACOB

Bases as plant stimulants and the pickling of seed with solutions of bases and other substances. T. BOKORNY. *Z. Pflanzenernähr. Dungung* 4A, 178-90(1925).— $NaOH$ ,  $KOH$  and  $NH_4OH$  were injurious or stimulating to the germination of seeds and growth of plants according to the concn. In equal mol concn  $KOH$  was least harmful and  $NH_4OH$  most so. The optimum concn for stimulation varied with the species. A. L. MEHRING

Growth of potato plants in sand cultures treated with the "six types" of nutrient solutions. E. S. JOHNSON. Maryland Agr. Expt. Sta., *Bull.* 270, 54-86(1924)—In expts with potato plants in sand cultures there is a direct relationship between growth and the presence of nitrogen in the nutrient solns.  $Mg(NO_3)_2$  was not as effective as  $KNO_3$  or  $Ca(NO_3)_2$ . Mg in high concn was toxic. Plant growth was best in the solns. contg. the following atomic proportions: N 4 to 6; P 2 to 4; K 2 to 4; S 1 to 2; Ca 3 to 1; Mg 2 to 1. The growth of the plants as influenced by percentages of P, N and K in commercial fertilizers and in field soils. J. J. SKINNER

Synthetic farmyard manure. F. HARDY. *Trop. Agr. (Trinidad)* 2, 108-9(1925).—It is claimed that the amt. of atm N fixed in the manuf. of synthetic manure is considerably less than formerly believed. In large-scale operations the max gain in N was 0.156%. A. L. MEHRING

Alkaline chlorosis of the vine. U. PRATOLONGO. *Atti acad. Lincei* [vi], 1, 319-22 (1925)—There is no casual connection between high alk. of the soil or its ten-

dency to produce chlorosis and the amts. or state of division of the  $\text{CaCO}_3$  which it contains B. C. A.

**Manganese as a cure for chlorosis of spinach.** F. T. McLEAN AND B. E. GILBERT. *Science* 61, 636-7(1925).—Spinach suffering from chlorosis and retarded growth, although planted in a soil receiving a complete chem. fertilization and moderately manured, was treated, at the rate of 9 l. per 30 ft. of row, with 0.02%  $\text{FeSO}_4$ , 0.004%  $\text{MnSO}_4$ , 0.05%  $\text{NH}_4\text{NO}_3$ , 0.1%  $\text{K}_2\text{SO}_4$ , 0.2%  $\text{K}_2\text{HPO}_4$ , 0.02% ferric  $\text{NH}_4$  citrate, 0.02% citric acid and manure leachings. Of all treatments only the Mn had any effect, and caused a definite improvement in 4 days, while at the end of a week normal growth with a bright green color had been resumed and the yield was increased 40%. Since 5 p. p. m.  $\text{H}_2\text{SO}_4$  caused no improvement it is concluded that Mn is the active agent in this case P. R. DAWSON

**Stinking-smut of wheat. II. Field experiments on control.** J. C. NEILL. *New Zealand J. Agr.* 30, 302-13(1925); cf. C. A. 18, 437.—Complete control of low and medium infections of stinking-smut of wheat (*Tilletia tritici*) was obtained with the following treatments: Cu carbonate dust;  $\text{CuSO}_4$ , formalin and hot- $\text{H}_2\text{O}$  immersion; and immersion in a soln. of Clarke's Wheat Protector, a proprietary fungicide. None of these treatments gave complete control in highly infected seed. The  $\text{CuSO}_4$ , formalin, hot- $\text{H}_2\text{O}$ , and proprietary treatments had a depressing effect on germination of the seed and the vigor of the plants while  $\text{CuCO}_3$  did not. Dipping in lime water before and after treatment with  $\text{CuSO}_4$  slightly reduced the effectiveness of the soln. in controlling the smut and also reduced the damage to the seed. Complete control in all cases of infection was obtained by treatment with the org. Hg compds. Uspulum, Germisan and Semesan; the first 2 compds. increased germination and the vigor of the plants while the latter had no effect. K. D. JACOB

**Report of insecticides and fungicides.** J. J. T. GRAHAM. *J. Assoc. Official Agr. Chemists* 8, 333-43(1925).—A report dealing with the development of methods for analysis of oil spray preps., either soap emulsions, non soap emulsions, or miscible oils. P. R. D.

**Some aspects of research on insecticides and fungicides.** C. M. SMITH. *Chemistry and Industry* 44, 417-20(1925).—This is a discussion of the results of research on insecticides and fungicides from the chem. standpoint. The need of further investigation of lime-sulfur solns., Bordeaux mixt., hellebore, quassia, cubebs and other plant products is indicated. The problems which await solution are: stability of insecticides and fungicides in storage, compatibility of spray and dust mixts., etc., the development of new materials, the study of the effect of an insecticide on the insect and on foliage, the safety of foods which have been sprayed or fumigated, the odorous substances in plants which attract insects, the improvement of the suspension, spreading and adherent qualities of a spray, elec. charges on substances in suspension and in the form of dusts, investigations on the size of dust particles, and various chem. problems connected with the application of insecticides and fungicides. The needs for improved methods of analysis of insecticides and fungicides are also discussed. C. H. R.

**The manufacture of insecticides and fungicides.** R. N. CHIPMAN. *Chemistry and Industry* 44, 421-2(1925).—The factory production of Paris green and Ca arsenate are discussed in addn. to certain economic phases of the insecticide industry. C. H. R.

**The pear midge.** Further observations and control with calcium cyanide. DAVID MILLER. *New Zealand J. Agr.* 30, 220-4(1925).— $\text{Ca}(\text{CN})_2$  applied on the ground beneath the trees in min. doses of 1.5 lb. per 200 sq. ft. gave complete control of pear midge (*Perrisia pyni*) larvae hibernating in the ground. Larvae of the cicada, and schneumon and muscid flies were apparently unaffected K. D. JACOB

Reducing ores [for fertilizers] (Brit. pat. 227,435) 9.

WHITNEY, MILTON: Soil and Civilization. New York: D. Van Nostrand Co 278 pp. \$3.00. Reviewed in *Ind. Eng. Chem.* 17, 876(1925).

**Phosphatic fertilizers.** F. L. SCHMIDT AND A. MESSERSCHMIDT. Brit. 227,217, Oct. 18, 1923. Phosphate rock is heated to a sintering or fusion temp. with a "considerable proportion" of K. Mg carbonate with or without soda or phonolite, leucite or feldspar.

**Phosphatic fertilizer.** CHEMOTCENT INSTYTUT BADAWCZY. Brit. 227,447, Jan. 7, 1924. Powd. coal mixed with ground mineral phosphate is burned, e. g., to heat steam

boilers. The phosphate is thus converted into a sol. form resembling Thomas meal and its soly may be further increased by adding gypsum to the mixt.

## 16—THE FERMENTATION INDUSTRIES

C. N. FREY

The yeasts of lambick. HUBERT KUFFERATH. *Chimie et industrie* 13, 890-900 (1925); cf. C. A. 16, 3363.—A review of the work done on lambick (a heavy Belgian beer) yeasts, describing more particularly the work carried out by K. in sepg. and identifying the organisms which play an essential part in the fermentation. A. P.-C.

Chemical reactions during the kilning of malt. H. LÖCHERS AND S. NISHIMURA. *Z. Ges. Brauwesen* 47, 61-6 (1924); *Wochschr. Brauerei* 42, 7-11 (1925).—Observations were made on the phys. and chem. changes during kilning of three types of malt, viz., a pale malt kilned at low temp., a pale malt kilned at the usual temp. and a dark malt. The following were observed during kilning: loss of  $H_2O$ , increase of corn wt. and growth and subsequent shrinkage of acrospire, percent of mealty corn compared with vitreous, total N, sol. N, coagulable N, amino N, changes in acidity, amount of invert sugar, enzyme content, and the evolution of  $CO_2$ . B. C. A.

Fermentation and iron salts. P. HODEL AND N. NEUENSCHWANDER. *Biochem. Z.* 156, 118-23 (1925).—The accelerating action of ferrous and ferric salts on yeast fermentation is regarded as involving the formation of a ferriphosphate. Velocity curves of  $CO_2$  production and the influence of Fe salts on  $CO_2$  production are presented. F. A. CAJORI

Some properties of fermentation vinegars and artificial vinegars whereby they may be distinguished by analytical means. U. PRATOLONGO. *Ann. chim. applicata* 15, 72-87 (1925).—Methods are given for distinguishing vinegars made by dilg. commercial  $AcOH$  from those made from alc. It was found that industrial  $AcOH$  contains 20-30 mg. aldehydes calcd. as  $CH_3O$  per 100 g.; fermentation vinegars 320-400. Vinegars made from pure dild.  $AcOH$  did not reduce  $KMnO_4$  appreciably; whereas 100 cc. of alc. vinegar reduce 4-16 cc. of 0.1 N  $KMnO_4$  in approx. a min. at room temp. The reducing compd. is unknown and does not distil with the vinegar directly or with steam. There is also a wide difference between the reaction of the two classes of vinegars with I; detn. of the I no. is described. C. C. DAVIS

Differentiation between mistellas and naturally sweet wines. LUCIEN SEMICHON. *Ann. fals.* 18, 286-92 (1925); cf. C. A. 17, 3398; 18, 433.—A discussion of the interpretation of analytical results, more particularly from the standpoint of the French pure food laws and regulations. A. PAPINEAU-COUTURE

### Surface tension of brewery worts (KING) 11B.

Drying yeast. E. A. FULLER. *Brit.* 228,017, Feb. 8, 1924. The yeast is fed into the space between and adheres to the surfaces of 2 juxtaposed oppositely rotating drums which are internally heated. Dried yeast is removed from the drums by scrapers.

## 17—PHARMACEUTICAL CHEMISTRY

W. O. EMERY

Preparation of essential oil from Anserine vermifuge. J. PIÉRAERTS. *Bull. agr. du Congo Belge* 15, 656-76 (1924).—Methods of prepn. and properties of essential oil from Anserine vermifuge are given. M. S. ANDERSON

Constituents of some Indian essential oils. XIV. Essential oil from the seeds of *Zanthoxylum ovalifolium*. J. L. SIMONSEN. *Indian Forest Records* 11, 1-5 (1924).—The oil sepd. by steam distn., amounting to about 0.3% of the seed and husk, consists chiefly of myrcene and safrole. Palmitic acid and combined lower fatty acids and a liquid phenol are present in small quantities. XV. Essential oil from the seeds of *Juniperus communis*. *Ibid.* 6-9.—The yield by steam distn. is 0.2%; the oil differs from normal juniper oil, and resembles oil of savin, contg. about 50% of *d*-sabinene, but no  $\alpha$ -pinene. B. C. A.

Experiences in the standardization of insulin preparations. P. HART. *Biochem. Z.* 156, 86-96 (1925).—In the biological assay of insulin, in which the dose required to bring about hypoglycemia with spasms in rabbits is detd., the appearance of convulsions

is not a sufficient criterion. In a series of 30 animals, convulsions appeared in only 60% following insulin injection, though marked hypoglycemia was present in all of them.

F. A. CAJORI

**Detecting the adulteration of vanilla extract.** C. B. GNADINGER. *Am. Perfumer* 20, 268-9(1925).—Vanilla ext is usually adulterated in 4 ways, 1st by the addn. of coumarin, heliotropin, cinnamic acid derivs. or various perfumes; 2nd, when prepd. from exhausted or partly exhausted beans fortified with synthetic vanillin; 3rd, use of less than the standard amt of beans, and 4th substitution of the cheaper varieties of exts for the more expensive and better ones. A method is described for detecting Tahiti vanilla in vanilla ext., based on the fact that Tahiti beans contain anisyl alcohol while Bourbon, Mexican, Java and South American beans apparently do not. Dealcobolize 50 cc of the ext by evapg spontaneously before a fan to about 15 cc., dil with H<sub>2</sub>O to 50 cc and shake with 50 cc of Et<sub>2</sub>O in a separatory funnel. Wash the Et<sub>2</sub>O ext 3 times with 15-cc portions of 2% NaOH soln. and once with 15 cc of H<sub>2</sub>O. Evap before a fan and as soon as the Et<sub>2</sub>O is expelled dissolve the residue in 0.5 cc. of alc. Add 2 to 3 drops of the alc. soln. to 2 or 3 cc. of concd H<sub>2</sub>SO<sub>4</sub> in a test tube, mix, and if Tahiti vanilla ext. is present a deep permanent red color, due to the presence of anisyl alcohol, develops immediately.

W. O. EMERY

**Chrysarobin.** R. EDER AND F. HAUSER. *Arch. Pharm.* 263, 321-47(1925).—See C A 19, 2202

W. O. EMERY

**Siamese benzoin.** IV. FRIEDRICH REINITZER. *Arch. Pharm.* 263, 347-58 (1925) cf C A 9, 121.—The amorphous foundation mass arising from the prepn. of crystalline benzoate from Siamese benzoin is amorphous coniferyl benzoate.

W. O. EMERY

**Evaluation and judging of storax.** P. BOHRISCH. *Arch. Pharm.* 263, 359-62 (1925).—Several methods for the detn. of constts are discussed, notably those of Dieterich, Jonsson, Ahrens, Hill and Cocking, and that of the Ger. Pharm. In estg the acid, ester and sapon. nos. Dieterich's method is favored, while the cinnamic acid is preferably detd. via Hill and Cocking.

W. O. EMERY

**Investigation of drugs and galenicals.** WILLY PEYER. *Pharm. Monatsh.* 6, 97-105(1925).—An address portraying the present status of drug research of crude and refined products, notably preps. of digitals.

W. O. EMERY

**Protargol and argentinum proteinicum.** J. MINDES. *Pharm. Monatsh.* 6, 106 (1925).—Descriptive.

W. O. EMERY

**New method for the estimation of yohimbine in yohimbe bark.** R. A. FELDHOFF. *Pharm. Ztg.* 70, 864(1925).—Moisten 50 to 100 g. of the powd. sample (No. 5 sieve of the Pharmacopeia) with a 10% crystd. Na<sub>2</sub>CO<sub>3</sub> soln. in a large porcelain evapg. dish, stirring the while with a spatula, allow to dry in a moderately warm atm., transfer to the extn. cylinder of a Soxhlet app. and connect with the distn. flask contg. 2 g. crystd. C<sub>12</sub>H<sub>22</sub>O<sub>4</sub> and 50 cc of H<sub>2</sub>O. Ext. with di- or trichloroethylene, in amt. sufficient to evacuate the extn. cylinder 5 or 6 times. On exhaustion of the drug, distil off the org. solvent, transfer the residual aq. soln. of the alkaloidal oxalate to a separatory funnel, add NH<sub>4</sub>OH soln. to liberate the alkaloids and ext. with 50, 20 and finally 10 cc. of Et<sub>2</sub>O. Dry the united Et<sub>2</sub>O portions over CaCl<sub>2</sub> or Na<sub>2</sub>SO<sub>4</sub>, filter into a thick walled beaker and ppt. the total alkaloids by the addn. of alc. HCl. Pour off the acid liquid, wash twice with Et<sub>2</sub>O, add 30 cc. of pure dry AcMe, rub the thick sirup with a glass rod to induce crystn., and soln. of secondary alkaloids; the yohimbine-HCl remains undissolved. Let stand 24 hrs. in the refrigerator, collect the crystals on a weighed filter, wash first with pure AcMe and finally with Et<sub>2</sub>O, then dry at 102° to const. wt. The weighed product is almost colorless, m. 286°, and is obtained in a yield of 1 to 1.5%.

W. O. EMERY

**Bio-assay of thyroid.** REM HENR. *Pub. Health Repts.* 40, 1461-6(1925).—The following suggestions, based on exptl. evidence, are offered: that (1) the assay of thyroid be based primarily upon the I content; (2) simple chem. tests be included for the detection of non-thyroid I; (3) in cases where a physiological test is desirable, the acetone-trile test as modified by Ström be used, but that the dosage be based upon the I content of the prepn. to be examd.; (4) the standard be a prepn. of thyroid of known origin contg. 0.2% of I; (5) physicians be urged to use thyroid of known I content and that they be requested to collect further data on the relation between the I content of different samples of thyroid and their effect upon the basal metabolism in cases of hypothyroidism.

W. O. EMERY

**Standardization of pollen extracts by the complement-fixation test.** CHAS. ARMSTRONG AND W. T. HARRISON. *Pub. Health Repts.* 40, 1466-72(1925).—The complement fixing property of ragweed pollen exts. is due to a labile reaction, is one of the first properties of the ext. to deteriorate, and its rate of deterioration bears no definite re-

lation to the rate of deterioration of that portion of the ext. which causes shock. The complement-fixing property of ragweed pollen ext. is a non-essential attribute insofar as the value of the ext. for treatment is concerned. Complement fixation as a means of standardization of ragweed pollen exts. should be applied only to exts. of stable antigenic nature, which, however, should be tested soon after extn. is completed. Complement fixation for standardization of ragweed pollen exts. which are not stable in antigenic properties is fraught with danger, because overdosage may result, for some exts. which are relatively unstable as regards their complement-fixing properties may lose the latter, while their ability to cause shock is relatively unaltered. W. O. EMERY

**Standardization of thyroid preparations.** REID HUNT *Arch. Intern. Med.* 35, 671-86(1925).—"The physiological activity of thyroid preps. as detd. by the McCN test on mice and by clinical observations was found to be closely parallel to the I content. Little or no physiologically inactive I was found by these tests in the thyroids of adult animals. (Some was found in fetal glands.) Very small quantities of non-thyroid I in adulterated thyroid preps. could be detected by the McCN test. Very few of the thyroid preps. on the market comply with the U. S. P. standard, they vary greatly in physiologic and therapeutic activity." I. GREENWALD

**The increase of free fatty acids in castor oil.** WM. PARTRIDGE *Analyst* 50, 284(1925).—"The Brit. Pharm. restricts the amt. of free fatty acids in castor oil to an acid value of not more than 4. Fifteen samples of castor oil were examd. and then allowed to stand for 4-38 months. The results show that a pharmacist may receive castor oil of good Brit. Pharm. quality and find within a few months that the acid value is too high. Thus a sample of 1.6 acid value changed to 5.3 after 14 months. W. T. H.

**The rose-oil industry in Bulgaria.** P. MARTELL. *Chem.-Zig* 49, 569-71(1925).—Rose culture and production of the oil are described. E. H.

**Experimental study of the methods for the demonstration of the specificity of ergot preparations.** K. E. SCHREGG *Z. ges. expil. Med.* 45, 368-84(1925).—A number of *Secale* preps. and synthetic compds. were tested for specific ergot action by a variety of methods and best results were obtained by a combination of the two methods following. The reversal of the action of adrenaline on the blood pressure of cats after the intravenous injection of the substance to be tested gives the best qual. test. The best quant. test is the method of Clark and Broom (*C. A.* 17, 3749) on the lessening or reversal of the effect of adrenaline on isolated rabbit uterus. The ergotamine ext. of Clark and Broom, which is a chem. entity, is used as a standard for comparison. HARRIET F. HOLMES

**Determination of essential oils in spices.** W. SCHUT. *Chem. Weekblad* 22, 344-7(1925).—"The official Dutch method for the assay of oil of cloves, which recommends steam distn. and weighing of the ether ext. of the distillate is cumbersome and unreliable. S. suggests 2 other methods: (I) The colorimetric method based on the red color produced by coned  $H_2SO_4$  in a very dil. soln. of the ether ext. of the drug; (II) volatilization of the essential oil by heating the ether ext. at 100-105° to const. wt. II is less exact than I but is also applicable to anise seed and cinnamon bark. MARY JACOBSEN

**Camphor oils. II. Reactions of Japanese acid clay to camphor white oil.** KASHICHI ONO. *Mem. Coll. Sci. Kyoto Imp. Univ.* 7, 349-60(1924), cf. *C. A.* 18, 1659, Venable, *C. A.* 17, 1454.—Camphor white oil ( $d_{20}$  0.8756,  $n_D^{20}$  1.4698,  $[\alpha]_D + 20.45^\circ$ , cineole 22.30%,  $d$ -limonene (b 175-7°,  $d_{20}$  0.8427,  $n_D^{20}$  1.4736,  $\alpha_D^{20}$  (1 dm.) + 95.22°), and cineole (b 175-7°,  $d_{20}$  0.9236,  $n_D^{20}$  1.4596,  $[\alpha]_D = 0$ ) were distd. in presence of Japanese acid clay; investigation of the distillate indicated that the main portion of the cineole changes into  $p$ -cymene and  $p$ -menthane, which is attributed to dehydration and polymerization, followed by decompn. at high temps. A. PAPINEAU COUTURE

**The cultivation of mints.** ETABLISSEMENTS A. CHIRIS *Parfums de France* No 28, 151-9(June, 1925).—Comparative tests were carried out with mint originating from Mitcham, some of which had been cultivated for some time in Northern France while the remainder had been recently introduced from Mitcham. The slight differences observed were presumably attributable to the difference in the length of time the plant had been cultivated in a warm climate. Yield tests carried out at intervals during cultivation have no abs. value from a com. standpoint, but are strictly comparable with one another. Max. oil yields (on the amount of plant used) were obtained just prior to the rapid growth which precedes flowering, after which the oil content of the plant falls fairly uniformly. Max. yields per hectare of oil having a high menthol content and delicate aroma are obtained by distg. plants harvested a few days before reaching full

bloom and at the beginning of the blossoming period. Plants cut later than this give an oil with even higher menthol content, but less delicate odor. The menthol content and  $d$  of the oil increase with the age of the plants from which it is obtained, while  $[\alpha]$  decreases, probably owing to changes in the terpene fraction of the oil. When the blossoms fall, there is a sudden increase in both free and combined menthol contents, and in  $[\alpha]$  and in  $d$ , due to increase in esterification caused by initial dehydration of the plant. The final stage of the evolution of the oil in the plant is represented by the oil obtained by distn. of leaves which fall naturally after the end of the growth of the plant: oil obtained in 0.75% yield had  $d_{15}^4$  0.9104,  $[\alpha]_D -31^\circ 46'$ , combined menthol 8.97%, total menthol 63.14%. These results are in contradiction with those of Charabot and Hébert (*Bull. soc. chim.* [3], 27, 221(1902)) and Rabak (*C. A.* 11, 1517), but in agreement with those of Russell (*C. A.* 19, 1753).

A. PAPINEAU-COUTURE

Constants of Russian oil of peppermint. B. RUTOVSKI and J. VINOGRADOVA. *Parfums de France* No. 28, 164-7 (June, 1925).—A sample of oil from the Poltava district obtained by distn. of plants cultivated locally had  $d_{15}^4$  0.9005,  $[\alpha]_D -21^\circ 15'$ , combined menthol 16.4%, free menthol 33.8%, menthone 18%, acid no. 0.9, 1 vol. sol. in 0.5 vol. of 90% alc., 5 compds. nil,  $f$  p.  $-5^\circ$ , b. p. 185-225°. With glacial AcOH it gives no color. Polenske's reaction (2 cc. of oil, 1 cc. glacial AcOH, 1 drop  $HNO_3$ ) gives a maroon, changing gradually to violet and finally to green.  $IR_2$ 's reaction (heating 1 cc. of oil in 5 cc. alc. with 0.45 g. sugar and 2 cc. HCl) gives a bluish violet color, gradually changing to dirty green. With chloral hydrate and HCl it gives a maroon color. Previously published consts. of Russian oils are tabulated, and the following are put forth as the normal consts. of good-grade oil:  $d_{15}^4$  0.9014-0.9150,  $[\alpha]_D -20^\circ$  to  $-27^\circ$ , combined menthol 6-15%, free menthol 41-51%, total menthol 49-56%, menthone 18-8%, acid no. 0.7-1.0. Comparison with the consts. of oils of other origins show it to be equal in quality to the highest grades.

A. PAPINEAU-COUTURE

Identification of natural cedrene. ETABLISSEMENTS A. CHIRIS. *Parfums de France* No. 28, 168 (June, 1925).—Semmler and Hoffmann's technic for the prepn., sepn., and purification of cedrene-glycol (*C. A.* 2, 106) has been simplified as follows: emulsify 5 g. of the sesquiterpene fraction (b. p. 115-6°,  $d_{15}^4$  0.9408,  $[\alpha]_D -50^\circ$ ,  $n_D^{20}$  1.50198, mol. refraction 64.29 (calcd. 64.45)) in a mixt. of 80 g.  $Me_2CO$  and 5 g.  $H_2O$ , add 5 g. of pulverized  $KMnO_4$ , during about 1 hr., agitating continually, and keeping at 30-5°, after complete reduction of the  $KMnO_4$  (effected eventually by addn. of a few drops of alc.) drain off the liquid, wash the Mn oxides with a little  $Me_2CO$ , add 20 cc.  $H_2O$  to the combined washings, evap. the  $Me_2CO$  on the water bath, place the aq. residue and supernatant only layer in a sepg. funnel, add about 50 cc. petr. ether (b. p. 60-80°), shake, and let stand without removing the stopper. In from a few min. to two hrs. the cedrene-glycol,  $C_{15}H_{24}O_2$ , crystallizes from the petr. ether as fine, white needles, recrystd. from  $Me_2CO$ , m. 167.5-168° (instead of 160° given by Semmler and Hoffmann). Cedrene-glycol obtained by oxidizing oil of cedar in the same way m. 167-167.5°, and a mixt. of the 2 products has the same m. p. The deta. can be carried out on 1-2 g. of cedrene and takes about 3 hrs.

A. PAPINEAU-COUTURE

Citral, irones and ionones. L. V. DOUAY. *Rev. parfumerie* 5, 168-70 (1925).—Brief review of the chemistry of the citrals, and of the derivation from them of the irones and ionones.

A. PAPINEAU-COUTURE

Constants of oil of sweet orange and oil of mandarin orange from the 1923 crop in Sicily and Calabria. L. BONACCORSI. *Riv. ital. ess. profum.* 7, 26-8 (1925); *Parfums de France* No. 28, 173-4 (June, 1925).—A no. of analyses are tabulated, showing no abnormal results in the consts.

A. PAPINEAU-COUTURE

Oil of "*Ptychotis verticillata*" Duby (D. C.). VALENTINO MORANI. *Riv. ital. ess. profum.* 7, 25-6 (1925); *Parfums de France* No. 28, 175 (June 1925).—Flowering plants harvested near Palermo at the end of July 1923, gave a 0.809% yield of oil with  $d_{15}^4$  0.92378,  $[\alpha]_D 5.11^\circ$ ,  $n_D^{17}$  1.5027, acid no. 1.9, ester no. 0, sol. in 1.8 vol. of 80% alc. at 20°, incompletely sol. in 20 vol. of 70% alc. at 20°. The oil becomes turbid on standing, and a stearoptene settles out. The phenol content (vis 5% NaOH) is 42.3%, consisting exclusively of thymol (phenylurethan m. 105.5-106.5°) without any carvacrol.

A. PAPINEAU-COUTURE

Sicilian oil of mint. V. MORANI. *Riv. ital. ess. profum.* 7, 65-7 (1925); *Parfums de France* No. 28, 175-6 (June, 1925).—M. confirms Pellini (*C. A.* 18, 146) to the effect that oil of *Mentha pulegium* var. *hirsuta* Guss. contains *paperitone*, instead of pulegone, which is present in oil of *Mentha pulegium* L. It has the following consts.:  $d_{15}^4$  0.92035-0.9253;  $[\alpha]_D 1.08^\circ$  to  $10.65^\circ$ ;  $n_D^{18}$  1.4657-1.4707; soly. at 20°, in 70% alc. 1.6-1.7 vol.,

in 80% alc. 0.8 vol.; yield of oil, from the fresh plant 0.693–0.947%, from the dried plant 1.080–1.139%; acid no. 0–0.8; ester no. 3.1–9.5; esters (as menthyl acetate) 1.09–3.36%; Ac no. 6.5–27.3; alcs., free 0.95–5.02, total 1.82–7.67; ketones (*via* Burgess) 54.5–49.66%. The ketones were extd. *via* sulfite, on the one hand, and with bisulfite and alc., on the other, and in both cases the regenerated ketone was identified as piperitone, the one extd. hot with sulfite being inactive (probably as a result of racemization), and the one extd. cold with bisulfite being *l*-rotatory. The former was identified by its  $\alpha$ -semicarbazone, m. 224–5°,  $\beta$ -semicarbazone, m. 174–5°, oxime m. 118–9°,  $\alpha$ -oxaminooxime, m. 171.5–172°,  $\beta$ -oxaminooxime, m. 187–8°, benzylidene deriv., m. 60–1°, and dehydrogenation into thymol (phenylurethan m. 106°). Two new derivs. of piperitone were prepd.: the semicarbazone, m. 217°, practically insol. in alc.; and the hydrazone of piperitone-phenylcarbamie acid, m. 193.5–194°, giving either  $\alpha$ - or  $\beta$ -semicarbazone on boiling with  $\text{PbNH}_2$ . The non-ketonic portion of the oil of mint had  $d_{15}^{20}$  0.90529,  $[\alpha]_D^{20}$  65.51°.

A. PAPINEAU-COUTURE

Origin of essential oils in plants and their relation to their constituents. RINA ASTENGO. *Riv. ital. ess. profum.* 7, 5, xi, xv (1925); *Parfums de France* No. 28, 175 (June 1925).—Starting from the fact that most of the constituents of essential oils contain 5, 10 or 15 C atoms, A. supposes that the higher compds are derived from isovaleraldehyde by condensation of the latter. The isovaleraldehyde would be due to oxidation of  $\text{AtmOH}$ , which is considered to be the compd. from which the essential oils are formed. The isovaleraldehyde condenses into isocitronellal, which isomerizes into rhodinol, citronellal and geraniol, which in turn are converted into rhodinol, citronellol, linalool, menthone, isopulegol and citral. A has succeeded in identifying the 3 basic compds. (valeric acid, valeraldehyde and  $\text{AtmOH}$ ) in all the citrus oil. Some or all of them have also been identified in oils of eucalyptus, citronella (Java), petitgrain (Paraguay), and spike

A. PAPINEAU-COUTURE

Benzyl citrates (Brit. pat. 227,232) 10. Cod-liver oil (Brit. pat. 227,474) 27.

Medicinal arsenic compounds. OSTRO-PRODUCTS CORPORATION OF AMERICA. Brit. 227,874, July 18, 1923. An aq. soln. of *p*-hydroxy-*m*-aminophenylarsenious oxide is added to an acidulated MeOH soln. of dihydroxydiaminoarsenobenzene hydrochloride, the soln. pptd. by ether, and the ppt. purified by soln. in MeOH and repptn. by ether; or, other described processes are followed for obtaining  $\text{H}_2\text{O}$ -sol. therapeutic products from compds. contg. As and O directly linked together by bonding with 4,4'-dihydroxy-3,3'-diaminoarsenobenzene-HCl or with Na 4,4'-dihydroxy-3,3'-diaminoarsenobenzene-*N*-methylenesulfinate as a protective colloid.

Veterinary medicine. F. E. RALPH. Brit. 227,713, June 6, 1924. A prepn. for prevention and cure of contagious abortion in cattle consists of Cu acetate and  $\text{CuSO}_4$  ground up with sperm oil or other fish oil.

## 18—ACIDS, ALKALIES, SALTS AND SUNDRIES

FRED C. ZEISBERG

Alkali, etc., works. J. W. YOUNG. *Sixty-first Ann. Rept.* 1924, 31 pp.—A rept. of conditions in England, Wales, and Scotland as regards noxious effluent gases from manufg. plants, such as alkali and Cu, cement,  $\text{H}_2\text{SO}_4$ ,  $\text{Cl}_2$ , chem. fertilizer, HCl, tar, etc. In general, conditions are better than in previous years. Treatment of effluent, spent liquors from the distn. of ammoniacal liquor is discussed in continuation of the 60th annual report (C. A. 18, 2945).

W. H. BOYNTON

Atmospheric nitrogen fixation. E. A. LOV. *Smithsonian Report* for 1923, 203–22 (1925).—A very brief general review of present com. methods of N fixation. R. L. D.

The fixation of atmospheric nitrogen. J. M. BRAHAM. *Trans. Am. Electrochem. Soc.* 48 (preprint)(1925).—B. briefly discusses the growth and trend in N fixation, the relation of power to fixation, the N products being made available to agriculture, the part which fixed N now plays in the world's total inorg. N production and the present state of fixation in the U. S. Cyanamide as such is not entirely satisfactory as a fertilizer. The synthetic  $\text{NH}_3$  process is the most important of all today. Over  $\frac{2}{3}$  of the total N fixed is by the  $\text{NH}_3$  process. The production of electrolytic H is a new development from the standpoint of N fixation. H is also produced as a secondary product by one of the electrochemical factories manufacturing P and  $\text{P}_2\text{O}_5$ . The various fer-

utilizer products from air N processes are briefly discussed. Chilean nitrate continues to be a very strong competitor. C. G. F.

Phenomena in the electric arc process of nitrogen fixation. S. KARRER. *Trans. Am. Electrochem. Soc.* 48 (Preprint)(1925).—The elec. arc process of N fixation has been a com. success in Norway, although the cost of production is very high. Only  $2\frac{1}{2}\%$  of the total energy consumed by the process is resident in the NO formed. However, it appears possible to increase this low yield after a more complete understanding of the phenomena which occur in the elec. discharge through air. The following phenomena are discussed at length: dissociation of  $O_2$  and  $N_2$  mols. into neutral atoms; ionization within the arc; excitation; radiation; energy transfer. C. G. F.

The manufacture of sodium nitrite by the arc process. H. K. BENSON. *Trans. Am. Electrochem. Soc.* 48 (Preprint)(1925).—The American Nitrogen Products Co. of Seattle is operating commercially a process for the fixation of N by the arc. A vast amt. of exptl. and development work was necessary. The electrodes, in particular, required very special study. Today the plants are producing 4-5 tons of  $NaNO_2$  per day. The gases from the arc are absorbed in a soln. of  $Na_2CO_3$ , the soln. is concd. and the  $NaNO_2$  crystals are removed by centrifuging. No details of the elec. app. are given. C. G. F.

The synthesis of ammonia by the Claude process. H. SALMANG. *Z. Ver. deut. Ing.* 69, 753-5(1925).—A discussion of the  $NH_3$  equil. and a brief description of the various technical phases of the Claude process. J. A. ALMQUIST

Absorption of ammonia in towers. O. L. KOWALKE, O. A. HOUGEN AND K. M. WATSON. *Chem. Met. Eng.* 32, 443-6(1925).—The general formula expressing the rate of  $NH_3$  absorption in terms of the transfer coeff. "ka" is  $W = (ka) V \Delta P_m$ , where  $W$  = lb of  $NH_3$  absorbed per min.,  $V$  = vol. of tower packing in cu. ft., and  $\Delta P_m$  = mean vapor pressure difference of  $NH_3$  between the gas and liquid phase throughout the tower. Experimentally detd. values of the transfer coeff. for various concns. of  $NH_3$ , rates of gas flow, rates of water flow and packing materials are given. The range covered is typical of operating conditions in the gas and coke industry. J. A. ALMQUIST

Absorption of ammonia in towers. O. L. KOWALKE, O. A. HOUGEN AND K. M. WATSON. *Chem. Met. Eng.* 32, 506-10(1925); cf. preceding abstr.—It is concluded from the exptl. work that the rate of  $NH_3$  absorption depends primarily upon the rate of diffusion of  $NH_3$  through the gas and that the resistance of the liquid film is negligible by comparison. The theory is advanced that the rate of absorption of  $NH_3$  and similar gases is controlled by this diffusion factor and a water distribution factor which is a function of the packing and the rates of water and gas flow. The total surface of the tower packing is of less importance than the position of the surfaces and the best packing is that which produces the greatest agitation of the gas in direct contact with the water surface. J. A. ALMQUIST

A direct synthetic ammonia plant. F. A. ERNST, F. C. REED AND W. L. EDWARDS. *Ind. Eng. Chem.* 17, 775-85(1925).—A discussion of the engineering design of equipment for a plant of 3 tons daily capacity, based on information acquired at the Fixed N Research Lab. Operation is of the circulatory type at 300 atm. with removal of the synthesized  $NH_3$  by direct liquefaction. The units described include a H-air burner, converters, condensers, special high-pressure fittings and a gas-circulating pump. J. A. ALMQUIST

Catalyst testing—the basis of new industries. D. H. KILLEFFER. *Ind. Eng. Chem.* 17, 789-92(1925).—Illustrated description of the catalyst-testing plant of La-zote, Inc., Wilmington, Delaware. The plant is designed to test  $NH_3$  synthesis catalyst at pressures from atm. to 1000 atm. and above at temps. up to 800° and at gas flows as high as 2,000,000 space velocity. Arrangements are made for the introduction into the system of gaseous impurities like CO,  $CH_4$ , and  $CO_2$ . Ten catalyst samples may be tested simultaneously. Gas pressures above 4500 lbs. per sq. in. are obtained by compression over  $H_2O$ . The plant is adapted to carry out catalyst testing for  $NH_3$  synthesis, but it may easily be converted to the testing of catalysts for other gas reactions. Accuracy of control and convenience of operation insure the value of the results obtained from it. R. L. DODGE

Refining natural salt cake. L. A. PALMER. *Chem. Met. Eng.* 32, 622-4(1925).—Refining of  $Na_2SO_4$  from the deposit at Soda Lake, Carrizo Plain, Calif., is described. E. H.

Cadmium: its occurrence, uses and production. ANON. *Bull. Imp. Inst.* 23, 181-95(1925). A. PAPINEAU-COUTURE

Manufacture of cadmium sulfides. L. A. SAUVAGEOT. *Rev. prod. chim.* 28, 397-400(1925).—Brief description of the com. processes, which consist essentially in

treating  $\text{CdCO}_3$  with  $(\text{NH}_4)_2\text{S}$  to obtain light shades, and treating  $\text{CdCO}_3$  with  $\text{Na}_2\text{S}$  to obtain the darker shades, the exact shade depending on the diln and temp at which the reaction is carried out.

A. PAPINEAU-COUTURE

Refined sulfurs: their manufacture and uses. C. A. NEWHALL. *Trans. Am. Inst. Chem. Eng.* 16, Pt. I, 163-83 (1924).—Comprehensive review of the development and present status of the S refining industry, with a critical summary of the properties and com. applications of the different forms of refined S.

A. P.-C.

Natural micas and reconstituted micas. BOUSQUET. *La nature* 53, i, 165 Suppl. (1925).—A description of the occurrence, phys. and chem. properties and uses of different types of micas and the prepn and subsequent reconstruction of thin lamellas to form micanite, etc.

C. C. DAVIS

Artificial precious stones. HANNS GÜNTHER. *Tech. Ind. Schweiz. Chem.-Ztg.* 1925, 101-10.—A review.

E. H.

Adsorption of poisons on a new plant charcoal "supra norit." E. LAQUEUR AND A. SLUYTERS. *Biochem. Z.* 156, 303-22 (1925).—A comparison was made of the adsorbing power of a commercial plant charcoal, supra norit, and an animal charcoal (Merks). Supra norit was found superior as an agent to adsorb such poisons as oxalic acid,  $\text{K}_2\text{C}_2\text{O}_4$ ,  $\text{HgCl}_2$ , strychnine nitrate, morphine sulfate, methylene blue and 1 from solns

F. A. CAJORI

Determining the value of oxygen-containing washing substances. KURT BRAUER. *Chem.-Ztg.* 49, 505-6 and 528-8 (1925).—Comparative expts. upon washing cloths under standard conditions with (a) Persil (an O-contg. cleansing agent), (b) soap and (c) soap powder, showed the superiority of Persil.

W. C. EBAUGH

Cleansing "ammonias." A. CHAPLET. *Tiba* 3, 707, 709 (1925).—A number of formulas are given for cleansing compds. contg.  $\text{NH}_3$ .

A. PAPINEAU-COUTURE

ANDÉAS, LOUIS EDGAR: *Verarbeitung des Hornes, Elfenbeins, Schildpatts, der Knochen und der Perlmutter.* 3rd ed. revised and enlarged. Vienna: A. Hartleben. 280 pp. R. M. 5, bound R. M. 6.

Sulfuric acid. H. HOWARD. U. S. 1,545,142, July 7. In the contact process of  $\text{H}_2\text{SO}_4$  manuf., hot burner gases are cooled out of contact with  $\text{H}_2\text{O}$ , the cooled gases are moistened, and are then successively filtered and dried.

Sulfuric acid. SOC. ANON. DE PRODUITS CHIMIQUES DE DROOGENBOSCH. Brit. 227,839, Jan. 19, 1924. Pure  $\text{H}_2\text{SO}_4$  of any desired degree of concn. is obtained by heating "oleum" and absorbing the liberated  $\text{SO}_3$  in  $\text{H}_2\text{O}$  or in dil. acid. An app. is described.

Chemical furnace of ceramic material. O. BEZANSON and M. S. MAXIM. U. S. 1,544,798, July 7. The furnace is adapted for making  $\text{HCl}$  from  $\text{NaCl}$  and  $\text{H}_2\text{SO}_4$ .

Ammonia synthesis. G. CLAUDE. U. S. 1,544,373, June 30. In  $\text{NH}_3$  synthesis from H and N under high pressure in the presence of a catalyst, the incoming gases are passed in heat-interchange relation to hot gases of the reaction, then through a conduit within the catalytic body and thence directly into the latter. Another portion of incoming gases is passed in contact with the interior wall of the pressure-sustaining tube used and thence passed into the catalytic body. Cf. C. A. 18, 2790.

Ammonia synthesis. L. CASALX. Brit. 227,491, Sept. 20, 1923. In prepg. catalysts for  $\text{NH}_3$  synthesis, magnetite or other natural or artificial oxide of Fe or of Co, Ni, Mn, Cr, Mo, W or U is heated in a current of O with C and either Al, Ca or Mg until violent ebullition ceases. The cooled product is broken up for use.

Ferric hydrate, etc. J. B. DU FAUR. Brit. 228,115, Jan. 21, 1924.  $\text{Fe}(\text{OH})_3$  is obtained from solns. contg. Fe salts by adding  $\text{CaCl}_2$  if the metals are not already in the form of chlorides, filtering off any  $\text{CaSO}_4$  formed, and then treating the chloride soln. with finely ground  $\text{CaCO}_3$  or lime and air. The process may be used to remove Fe from solns. of Cu, Co or other metals to purify them.

Barium and strontium hydroxides. B. C. STUER AND RHEINLANDE VEREIN CHEMISCHER FABRIKEN AKT.-GES. Brit. 227,666, March 10, 1924. A soln. of the sulfide is treated with  $\text{NH}_3$  or, for more complete conversion, with  $\text{NH}_3$  and caustic alkali.

Barium chloride. VEREIN FÜR CHEMISCHE UND METALLURGISCHE PRODUKTION. Brit. 228,165, Jan. 21, 1924. An aq. paste of raw Ba sulfide is mixed with half the equiv. amt. of  $\text{HCl}$  to convert half the Ba into chloride. The soln. is treated with alkali chloride in excess to convert the  $\text{Ba}(\text{SH})_2$  into chloride and salt out the latter. After sepn. of  $\text{BaCl}_2$ , the mother liquor contg. alkali hydrosulfide and chloride may be used with additional Ba sulfide for continuing the process.

Aluminum chloride. A. M. McAFEE U. S. 1,544,328, June 30 Bauxite or other Al-contg. material is treated with Cl in the presence of activated C.

Aluminum chloride from bauxite. A. M. McAFEE U. S. 1,543,934, June 30 Bauxite for use in  $AlCl_3$  manuf. is dehydrated at a temp. (preferably about  $370^\circ$ ) below that at which substantial shrinkage takes place and C is then catalytically deposited in its pores

Magnesia from dolomite. F. W. BROWN and G. L. AUSTIN U. S. 1,544,800, July 7  $CaCl_2$  is added to calcined dolomite, the mixt. is treated with  $H_2SO_4$  to form  $CaSO_4$  and  $MgSO_4$  which will react with the  $CaCl_2$  present to form  $MgCl_2$  and additional  $CaSO_4$ , and the pptd.  $CaSO_4$  is sepd. from the soln.

Calcium permanganate. R. E. WILSON, L. W. PARSONS and S. L. CHISHOLM. U. S. 1,544,115, June 30 Permanganic acid is neutralized and the resulting soln. is treated with  $CaSO_4$  to form Ca permanganate

Calcium arsenate. D. LOPEZ U. S. 1,544,250, June 30 A light fluffy Ca arsenate is produced in a single step by passing Cl into a mixt. of lukewarm  $H_2O$ ,  $As_2O_3$  and lime, and boiling the mixt. after reaction occurs to minimize the production of sol. arsenates.

Lithium salts. H. WEIDMANN U. S. 1,544,114, June 30. A soln. contg. a Li salt such as  $Li_2SO_4$  together with  $CaSO_4$  or other impurities is treated with  $K_2CO_3$  or other alkali metal salt of an acid of which the Li salt is less sol. than the Li salt in the soln., in quantity insufficient to ppt. the less sol. Li salt, pptd. impurities are sepd., and the Li salt is recovered from the soln.

Clarifying tin and titanium solutions. C. WEIDMANN and J. BLUMENFELD Brit. 227,143, Aug. 3, 1923 Sn and Ti solns. are clarified by adding a colloidal metal sulfide of opposite sign to that of the colloidal matter to be removed; e. g., a soln. of Ti sulfate may be treated with  $As_2O_3$  and then with Fe sulfide to ppt. the As as sulfide. Solns. of Th hydroxide in HCl may be clarified by albumin or other colloids

Recovering silver from solutions. R. BORN. U. S. 1,545,032, July 7. A soln. contg. Ag thiosulfate is treated with Na sulfide or other sol. sulfide, while alkyl. is maintained, to ppt. Ag sulfide

Vanadium from phosphoric acid solutions. F. LAIST. U. S. 1,544,911, July 7. Ferrocyanide of Ca or other sol. ferrocyanide is added to a phosphoric acid soln. contg. V to ppt. the latter and the ppt. is treated with the hydroxide of the alk. earth to regenerate the ferrocyanide.

Hydrogen from steam and carbon monoxide. G. L. E. PATART Brit. 228,153, Jan. 21, 1924 In gaseous reactions such as the catalytic manuf. of H from  $H_2O$  vapor and CO, heat and surplus  $H_2O$  vapor are recovered in a special vertical column app. through which  $H_2O$  is continuously circulated

Decolorizing carbon. C. J. GAMBEL. U. S. 1,543,763, June 30 Fibrous rice material such as rice hulls is charred and the charred material is treated with boiling NaOH soln. or other alkali to remove resins and a substantial portion of the silica present. Substantially all the alkali is removed from the charred material, and the remaining alkali is neutralized by treatment with  $CO_2$  or other acid anhydride the b. p. of which is below  $100^\circ$ . Any excess of acid anhydride is removed by heating Cf. C. A. 19, 1477.

Clay for filtering and decolorizing. E. C. BIERCE. U. S. 1,544,210, June 30. Colloidal clay for use in filtering or decolorizing is prepd. by drying the clay lumps as they come from the quarry, without preliminary grinding or addn. of  $H_2O$ , to reduce the  $H_2O$  content to 12%, adding  $H_2SO_4$  or other inorg. acid 4%, drying to a free  $H_2O$  content of 5%, coarsely comminuting, adding 1% of  $H_2SO_4$  or other inorg. acid, and screening to grade the product in different sizes

Purifying asbestos. R. DRAMBOUR U. S. 1,545,132, July 7. Rock carrying asbestos fiber is treated with a hot aq. caustic alkali soln. until the fibers sep. from each other and from associated impurities. The major portion of the liquid is then extd. and the moist mass is subjected to the action of an elec. current for the further sepn. and elimination of impurities associated with the fibers.

Stabilizing chlorinated lime. H. P. CADY. U. S. 1,545,394, July 7.  $Na_2CO_3$  and petroleum oil are added

Rotary kiln adapted for burning lime. C. J. TOMLINSON. U. S. 1,544,504, June 30. Salt-cake furnace. FARBERKE VORM MEISTER, LUCIUS & BRÜNING. Brit. 227,799, Jan. 18, 1924. In a salt-cake furnace of the type covered by Brit. 225,548 (C. A. 19, 1617) the acid is fed to the hearth through pipes through the muffle roof.

Fire-extinguishing compositions. G. A. GREGORY and MINIMAX, LTD. Brit. 227,936, Oct. 26, 1923 Fire-extinguishers are charged with  $CCl_4$  and  $HIOAc$  in one

compartment and the other compartment is charged with a foam-producing material such as "quilla," licorice ext., gum, or glue, and alkali.

Etched printing surfaces. W. STRAUB. Brit. 227,638, Jan. 31, 1924. Al or Al alloy printing surfaces are etched by a soln. of a Hg salt.

Detergent and polish for metals. M. W. GLEESON. U. S. 1,544,735, July 7. CCl<sub>4</sub>, 3, paraffin oil 5, rottenstone 16 and Venetian red 1 part.

Metal-cleaning composition. M. VIGANT. U. S. 1,545,210, July 7. A compn. for cleaning Ag or other metals comprises NaCN 14, (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> 2 and H<sub>2</sub>O 128 parts.

Material for stiffening box toes of shoes. A. L. CLAPP. U. S. 1,544,813, July 7. Cattle hair and chem. wood pulp (or other similar long and short fibers) are mixed with a thermoplastic compn. such as an aq. mixt. or emulsion of casein, rosin, gilsonite, montan wax and asphalt and the particles of the compn. are fixed on the fibers by pptn., e. g., by use of alum. The material is formed into sheets. U. S. 1,544,814 relates also to a box toe material contg. felted fibers, thermoplastic material and a metallic soap such as an Al or Ca soap.

## 19—GLASS, CLAY PRODUCTS, REFRACTORIES AND ENAMELED METALS

G. E. BARTON, C. H. KERR

Coloring glass by means of nickel. KITSUZO FUNA. *J. Japan. Ceram. Assoc.* No. 361, 430-44 (1922). *Chimie et industrie* 13, 99. —NiO gives a purple color to K glass and a brown color to Na glass, the color losing clearness when the quantity of Ni oxide is increased. The bivalent element which enters into the compn. of the glass has little effect, except Ba, which acts on the color. In borosilicates NiO gives a purplish pink. Oxidizing (KNO<sub>3</sub>) or reducing agents (K tartrate or As<sub>2</sub>O<sub>3</sub>) do not interfere with the production of the color.

Resistance of chemical glassware. C. E. KLAMER. *Chem. Weekblad* 22, 140-1 (1925).—Jena, Pyrex, Sphinx and Murano glass were tested by boiling with HCl, alkali and P<sub>2</sub>O<sub>5</sub>-H<sub>2</sub>SO<sub>4</sub> mixt. The individual differences were immaterial. B. J. C. v. d. H.

The resistance of some laboratory glassware to chemical reagents. D. MISLIACCI. *Ann. chim. applicata* 15, 87-91 (1925).—Two series of tests were made on Jena-Schott (white label) (I), Thuringian (II), Pyrex (Monti Milano) (III) and Murano 1922 (IV), one series with the new glass and the other with the same glass previously exposed to steam at 140°. In each series the glass was boiled 3 hrs. HCl, Na<sub>2</sub>CO<sub>3</sub>, NH<sub>4</sub>OH and NH<sub>4</sub>Cl and in the first series in H<sub>2</sub>O also. The resistance to the reagents before and after steaming at 140° decreased in the following order: before steaming: H<sub>2</sub>O, IV, III, II, I; steam at 140°, III, IV, I, II; 0.1 N Na<sub>2</sub>CO<sub>3</sub>, I, IV, II, III; 0.1 N NH<sub>4</sub>Cl, III, IV, I, II; 0.1 N HCl, III, I, IV, II; 0.5 N NH<sub>4</sub>OH, I, III, IV, II; total losses, I, IV, III, II; after steaming: 0.1 N Na<sub>2</sub>CO<sub>3</sub>, I, IV, II, III; 0.1 N NH<sub>4</sub>Cl, III and IV, I, II; 0.1 N HCl, I and III, IV, II; 0.5 N NH<sub>4</sub>OH, I, III, IV, II; total losses, I, IV, III, II. Pyrex, though it offers great resistance to heating and to shock, is unsuitable for use with alk. solns. Murano glass would be a satisfactory substitute for Jena if it were equally resistant to heating. Preliminary exposure to steam made all the glasses much more resistant to the chem. reagents; the total losses in mg. per dm<sup>2</sup> surface before and after steaming were I, 22.53, 10.74; II, 68.6, 34.02; III, 37.96, 33.21; IV, 29.6, 19.22. Such treatment is, therefore, recommended when the glassware is to be used in very accurate work. A survey of past work with 41 references is included.

The corrosion of glass surfaces. W. MOREY. *Ind. Eng. Chem.* 17, 389-92 (1925).—The mechanism of the corrosion of glass by water is complex, involving in its initial stages a probable miscibility of glass, regarded as an undercooled liquid, with water, and in its later stages the complete decompn. of the silicates. In interpreting the results obtained by the various methods of testing glass, the term "solubility" has no meaning, the results merely affording a measure of the rate at which the reactions take place. Great care must be taken to specify the conditions as the rates of reaction are peculiarly susceptible to them.

The photo-elastic constants of glass as affected by high temperatures and by lapse of time. F. C. HARRIS. *Proc. Roy. Soc. (London)* 106A, 718-23 (1924).—The stress-optical coeff. shows an increase with rise of temp. with the exception of an extra dense flint (PbO = 64.4%). Twelve glasses tested also showed an increase with lapse of time.

The manufacture and use of silica brick. H. SCHULING. *Chem.-Ztg.* 49, 508

(1925), cf. *C. A.* 19, 1038.—For a given temp. the time required for burning silica brick is detd. by the size of the particles and the structure of the quartzite used; e. g., the smaller the particles and the finer the structure (as observed with a polarizing microscope), the quicker the burning. This is altered by the presence of fluxes, such as  $\text{CaO}$ . To obtain a good product slow cooling, without access of cold air, is necessary; thus allowing for crystn. with max. stability. Finished brick must be preserved from moisture and freezing. Places where they may be used to advantage are mentioned.

W. C. ERAUGH

Research on enamel raw materials. M. C. CHOW. *J. China Soc. Chem. Ind.* 3, No. 1, 9-38(1925).—Analyses.

W. H. ADOLPH

Recent developments in the production and consumption of abrasive garnet. W. M. MYERS AND C. O. ANDERSON. *Bur. Mines, Repts. Investigations* No 2691, 11 pp (1925).

E. H.

Refractories and coke-oven technology (JUNIUS) 21. Furnace for melting glass, enamel in crucibles (U. S. pat. 1,545,008) 1.

Glass batch. O. W. HILBERT. U. S. 1,543,770, June 30. Finely powd. raw materials of a glass batch are mixed and heated sufficiently to produce small granules each of which is composed of the desired proportions of the raw materials.

Annealing glass sheets. E. B. LEMARE AND PILKINGTON BROS., LTD. *Brit.* 227,249, Nov. 19, 1923. Mech. features and temp. control in continuous sheet glass manuf.

Furnace for glass manufacture. T. C. MOORSHEAD AND UNITED GLASS BOTTLE MANUFACTURERS, LTD. *Brit.* 227,939, Oct. 27, 1923.

Pottery. J. E. TAMS. *Brit.* 228,058, June 5, 1924. A semi porcelain material for pottery comprises ball clay 8, china clay 12 and powd. hydrated  $\text{Mg}$  silicate 3 parts, blunged together with  $\text{H}_2\text{O}$  into a slip. Cf. *C. A.* 18, 315.

Apparatus for testing pottery for defects of expansion differences and for resistance to chipping and breaking. W. POOMORE AND A. J. POOMORE. *Brit.* 227,139, July 12, 1923.

Fused quartz. E. R. BERRY. U. S. 1,544,293, June 30. A surface layer of about 0.005 in. thickness is removed from clear quartz which has been fused in the presence of C, to prevent the formation of striae when the quartz is fashioned into final form.

Refractory material for crucibles, etc. P. LINDSAY AND MORGAN CRUCIBLE CO., LTD. *Brit.* 227,270, Dec. 17, 1923. Crucibles or other refractory articles are made from a mixt. of clay, graphite and sillimanite or a similar compd. of alumina and silica, with or without sand, Si carbide or other ingredients.

Refractory heat-insulation. H. T. COSS. U. S. 1,544,433, June 30. Insulation adapted for use on high-temp. furnaces and kilns is produced by calcining fabricated bodies of a mixt. of diatomaceous earth, lime or other "catalytic inversion agent" and  $\text{H}_2\text{O}$ . The product consists principally of tridymite.

Down-draft brick kiln. O. M. REIP. U. S. 1,544,509, July 7.

Abrasive. H. R. POWER. U. S. 1,544,343, June 30. An abrasive adapted for grinding engine valve seats comprises particles of carborundum or similar material and an alga jelly product such as Irish moss, glycerol and  $\text{H}_2\text{O}$  and is free from alum or oil. Cf. *C. A.* 19, 2396.

## 20—CEMENT AND OTHER BUILDING MATERIALS

J. C. WITT

Fused cement. J. DAUTREBAND. *Chaleur et industrie* 6, 227-30(1925).—Brief review of its manuf. and properties.

A. PAPINEAU-COUTURE

A photometric method for magnesia in portland cement. W. E. HASKELL. *Cement Mill Section* 27, 101(1925).—Magnesia can be detd. with a Jackson photometer with accuracy sufficient for routine mill analysis.

RAYMOND WILSON

Quality of oil for surface oiling of earth roads and streets. F. L. SPERRY. *Proc. Am. Soc. Testing Materials* (Preprint) No. 50, June 1925, 1-9.—Tests carried out on 6 different earth (not gravel or macadam) roads in Ill., U. S. A., indicated that: semi-asphaltic and paraffin-base oils are superior to asphaltic-base oils on earth roads, because they resist emulsification and retain their life much longer in contact with the soil and  $\text{H}_2\text{O}$ ; reduced-pressure tar is a satisfactory oil for earth roads; binding qualities and

adhesiveness are secondary in importance to ability of the oil to resist emulsification and retain its life in contact with the soil; cut-back or mat-forming oils which develop their asphalt content by evapn. of lighter constituents after application are not well suited for earth roads; non-volatile and homogeneous oils penetrate better and more evenly than blended products, the latter tending to sep. when applied; the so-called "asphalt or solid residue test" is unsatisfactory as a basis of purchase or specifications for semi-asphaltic or paraffin oils for earth roads; but may be of some value to the chemist in establishing the identity and characteristics of unknown products.

A. PAPINEAU-COUTURE

Annual report of the agricultural chemist to government, Punjab (LANDER) 15.  
Ornamenting wood (Brit. pat. 227,202) 25. Iron and slag cement (Brit. pat. 227,837) 9.

Hydraulic bituminous cement. G. D. COLETTA. Brit. 227,966, Sept. 10, 1924. A compn. which may be used in the same way as port. cement comprises asphaltic bitumen 15-20, port. cement 80-75, lime 3-4 and  $\text{SiO}_2$  or other inert substance 2-1%.

Slag cement. GEWERKSCHAFT LUTZ III. Brit. 228,128, Jan. 21, 1924. Lime is added to the charge of a blast-furnace to produce a slag cement. O is supplied to the blast to obtain an increased temp. required by the use of the lime. Brit. 228,129 specifies enriching with O the air supplied to a gas generator from the residue of which a slag cement is to be made.

Drying cement slurry. J. S. PASTING. Brit. 227,977, Dec. 15, 1923. Mech. features.

Rotary cooler for cement clinker. P. T. LINDHARD. U. S. 1,545,055, July 7.

Cement kiln. C. NASEB. Brit. 227,444, Jan. 8, 1924.

Refractory concrete. TEHAFO TECHNISCHER HANDELS- U. FORSCHUNGS-GES. Brit. 227,679, April 8, 1924. A concrete resistant to heat and furnace gases is formed from cement 3, trass 1, and chamotte 11 parts, or equiv. materials.

Plaster. H. D. BAYLOR. U. S. 1,544,421, June 30. Port. cement, sand, finely divided shale or siliceous clay and fibrous material such as cattle hair are used with a hydrated natural cement and lime mixed with waxy or oily substances or other org. plastic water-repellant material.

Paving composition. H. A. BATTALIOU. Brit. 227,279, Jan. 11, 1924. Pavements, blocks, slabs, etc., are formed of a mixt. of sand 37,  $\text{CaCO}_3$  35, Fe oxide 15, Al silicate 12 and amorphous C 1 part, which may be used with aggregate and with bituminous material.

Artificial stone. J. W. LEDEBOER. U. S. 1,544,843, July 7. A sheet is formed from a sticky wet mixt. of hydraulic cement, fibrous material such as asbestos and  $\text{H}_2\text{O}$ , sprinkled with pulverized set cement and asbestos or other finely divided material and a plurality of thicknesses of sheets of this kind are united under pressure before they have set.

Rubber-faced tiles, building blocks, etc. G. O. CASE and NOVOCRETES, LTD. Brit. 227,153, Sept. 11, 1923. A rubber facing is backed with vulcanized spongy rubber and may also be provided with a further backing of calcareous, aluminous, shale or Mg oxychloride cement and fibrous material.

Rubber-faced wall coverings. V. LEFEBURE. Brit. 227,578, Nov. 26, 1923. A vulcanized hard rubber sheet (which may be decorated) is attached to a backing sheet of paper, canvas or cement. Rubber cement or a phenol- $\text{CH}_2\text{O}$  condensation product may be used for joining the 2 layers.

Porous building blocks, etc., from slags and glass refuse. F. NETTEL. Brit. 227,848, Jan. 15, 1924.  $\text{CaCO}_3$  or other gas-developing material is mixed with molten slag or glass refuse immediately before molding, to produce a porous product.

Magnesite blocks. DEUTSCH-LUXEMBURGISCHE BERGWERKS- UND HÜTTEN- AKT.-GES. Brit. 227,802, Jan. 16, 1924. Mixts. of  $\text{MgO}$  or magnesite with Fe, Fe ore, slag from puddling furnaces, rolling-mill scale or other Fe-bearing sintering agents are treated with an acid, base or salt, preferably an Fe salt, to effect uniform distribution of the sintering agent.

"Wood substitutes." E. DOUZAL. Brit. 227,419, Jan. 12, 1924.  $\text{MgO}$  is treated with HCl only partially to convert it into oxychloride and mixed with Ca caseinate contg. excess casein sufficient to combine with the free oxide. This product is mixed with a separately prepd. compn. formed by treating sawdust with Venice turpentine, rosin and spirits of turpentine and mixing with cork, asbestos, kapok or peat. Pb acc.

tate is added to the combined mixt and it is compressed in molds heated to about 40° for 6 hrs

"Wood substitutes," etc., for building purposes. P. MARPILLERO, L. LORENZETTI and I. MARZOLA. Brit 227,299, Feb. 15, 1924. Straw, sugar cane fiber, maize stalk fiber, wood shavings, waste from wine presses, etc., are given a preservative and fireproofing treatment with  $MgSO_4$  or Na silicate and then molded after admixt with a binder such as port cement, a Mg oxide compn. or plaster.

Preserving wood. A. M. HOWARD. Brit 228,119, Jan. 23, 1924. An emulsion of  $ZnCl_2$  soln. or other aq. preservative dispersed in a mixt. of asphaltic petroleum residue and asphaltic base crude oil, or in other oily preservatives, is forced into the wood.

Preserving wood. J. W. KITCHEN and V. LEFEBURE. U. S. 1,544,013, June 30. An aq. soln. for treating wood comprises a sugar sirup with the addn. of 1% of NaF and 1/4% dinitrophenolate and an additional carbohydrate such as dextrin to give a d. to the soln. of about 1.050.

Preserving wooden poles, posts, etc. P. J. HOWE and R. LEEDOM. U. S. 1,545,427, July 7. Wooden poles or the like are immersed at their lower ends in a tank contg. a 3%  $ZnCl_2$  soln. satd. with NaCl on which a layer of creosote is floating, at a temp. of about 105°.

## 21—FUELS, GAS, TAR AND COKE

A. C. FIELDNER

Synthetic petroleum and the national fuel. H. WINKLER and L. JACQUE. *La Nature* 53, 1, 325-7, 346-7(1925).—A review from the chem. standpoint of the liquid fuel problem, including a discussion of cracking and hydrogenation of petroleum, carbonization of oils and the possibilities of  $EtOH$  and  $MeOH$  as fuels. C. C. D.

The use of alcohol in motor fuels. FRITZWEILER. *Z. Spiritusind* 48, 207(1925).—F. discusses the methods for detg. the efficiency of motor fuels and compares the efficiency of mixts. of alc. and benzine with that of a high-grade fuel. Curves are given illustrating the results. C. N. FREY

The ignition of solid fuels with special reference to raw brown coals under large boiler units. CURT RÖHL. *Wärme & Kälte Tech.* 27, 107-10(1925).—R. describes 2 inclined grate furnaces—the Steinhöller grate (cf. Pradel, C. A. 19, 2402) and the Seyboth grate. The latter is composed of several sections, on each of which the rate of travel of the fuel and the draft may be separately regulated. Summaries of boiler tests are given. ERNEST W. THIELE

Gaseous or solid fuel for space heating? HUDLER. *Feuerungstechnik* 13, 181-2(1925).—The coke made in a gas plant should be deducted from the coal used before calcg. the heat efficiency, which will then work out at about 52%. Hence a coal stove having an efficiency of only 41% is as economical as a gas fire having an efficiency of 85%; the latter can never be profitable. ERNEST W. THIELE

New Zealand brown coals. Some leaching experiments with Avoca, Mossbank, and Coal Creek Flat coals. L. R. DUNN. *J. Soc. Chem. Ind.* 44, 274-5T(1925).—Samples of these coals, typical, resp., of a black lignite, a young pitch coal, and a retinitous brown lignite were (1) boiled with distd. water under a reflux condenser for 30 days; (2) extd. in a metal Soxhlet with distd. water for 90 days; (3) subjected in a vertical glass tube to slowly trickling 0.01 N  $H_2SO_4$  for 30 days; (4) a sample of the last one was rapidly stirred in 40 l. of distd.  $H_2O$  for 30 days with a stream of  $CO_2$  passing through the water. Seven tables of analytical data give the  $H_2O$  and ash in the coals before leaching; the effects on the % compn. of the ash of the different methods of leaching; the changes in the silica/alumina ratio; and the hygroscopic power of the dry coals. Water effected very appreciable changes in the character of each of the ashes, rapid reduction in alkalis was most noticeable, there being an actual increase in  $SO_3$  taken out as alkali sulfate due probably to hydrolysis and oxidation of S-contg. ulmic substances in the coals. Treatment with 0.01 N  $H_2SO_4$  lowered the % S considerably in 2 cases. There was a marked decrease of the ash % in all cases, especially noted with the  $H_2SO_4$ . The silica/alumina ratio in the ash was decreased by the water treatments and markedly increased by sulfuric acid.  $CO_2$  in soln. had no marked action on the ash of Coal Creek Flat coal, which suggests that the Ca is present chiefly as ulmic compds. and not as inorg. salts, also the protective influence of the very high resin content of this coal should be considered. W. W. HODGE

Note on the inorganic constituents of some New Zealand coals. H. O. ASKEW. *J. Soc. Chem. Ind.* 44, 276T(1925).—To ascertain the state of combination of some of

the mineral constituents in 3 New Zealand lignites, 100 g samples of the powd. coals were placed in 500-cc. pressure bottles with 400 cc of approx  $N/10$  soln. of  $Na_2SO_4$  or  $MgCl_2$ . The mixts. were shaken for 4 or 8 weeks at room temp. then filtered and the compos. of the filtrates detd. Tables give the % compn. of the ash of the original coals and the % of  $CaO$ ,  $MgO$ ,  $SiO_2$ ,  $SO_3$ , and  $Cl$  in the different filtrates. A large excess of  $Ca$  and  $Mg$  as compared with the other bases passed into soln. Some base exchange processes take place. In 2 cases  $Na$  replaced  $Ca$  and  $Mg$  in complex silicates, and possibly in free  $CaCO_3$  in one coal; in the 3rd series of expts.  $Mg$  displaced  $Ca$  and perhaps  $Na$ . No reduction of the sulfate solns. by the coal was observed. W. W. H.

The history of powdered-coal firing. E. MAASS. *Feuerungstechnik* 13, 224(1925). — A brief summary. ERNEST W. THIELE

The thermodynamic and economic basis of powdered-coal firing. ROBIN. *Braunkohle* 24, 241-50(1925). — Where  $F$  is the surface of the coal particle in sq. mm. and  $G$  its wt. in mg., the time  $Z$  in sec. required for combustion at a chamber temp. of  $1300^\circ$  has been found by expt. to equal  $1000/(F/G)^{1/2}$ , while if a d. of 1.2 and a cubical shape with side equal to  $a$  mm. be assumed, the expression reduces to  $Z = 1000/(5/a)^{1/2}$ . The influence of ash on this time is slight from the standpoint of its thermal effects (sp. heat and heat of fusion) but large in that it reduces the surface, although the above equation holds if allowance be made for this reduction of surface, in finely powd. material this effect tends to disappear since the mixt. approaches a mixt. of pure coal particles and inert ash particles, but for large pieces (a 400 g. briquet)  $Z$  was, resp., 27 min. and 42 min. for 7 and 50% ash. The above expressions apply, however, only to a powd. brown coal contg. 55.8% (volatile matter +  $H_2O$ ), and since the effect of gas evolution during combustion is large correction must be made for any large difference in these constituents. The higher the % fixed C the longer the burning time, so that for a fuel contg. 100% fixed C and  $Z$  calcd. must be multiplied by  $(1/0.442)^{1/2}$  or by 4.35, while for one contg. 25% total volatile matter instead of 55.8% the factor is  $(0.75/0.442)^{1/2}$  or 2.6. The capacity of the fire chamber may also be calcd.; let it equal  $B$  in kg. cal./cu. m./hr., where  $H$  is the lower heating value of the fuel in kg. cal./kg., and  $V$  the vol. of flue gas in cu. m. at fire-chamber temp./kg. fuel. Then  $B_{max.} = 3600 H/(VZ)$ , or since  $H/V$  has been found for C, mineral coal, and dry brown coal to equal within 1% of 84.0 the equation may be written  $B_{max.} = 338,000/Z$ ; these expressions hold only for 0% excess air; for 10.2% excess air the const. of the latter equation becomes 327,000, for 28% 313,000, for 64% 292,000, for 100% 278,000; the fire-chamber temps. corresponding to these various conditions are  $2030^\circ$  (0% excess),  $1900^\circ$ ,  $1700^\circ$ ,  $1400^\circ$  and  $1200^\circ$ ; the foregoing figures are representative of the lengthy tabulation given. In practical calcs. the application of these equations must be made by a series of approximations in order to arrive at a value of  $B_{max.}$  corrected for heat losses by radiation and conduction, the chamber temp. being fixed. These calcs. are discussed in detail with examples. WM. B. PLUMMER

Firing locomotives with powdered coal. P. WANGEMANN. *Feuerungstechnik* 13, 193-5(1925). — A discussion of various methods of improving these installations. Mills for each locomotive are recommended, because there is less danger of explosion in case of accident, and less danger of a general interruption of traffic. ERNEST W. THIELE

Coal mining in Utah. C. A. ALLEN. *Bur. Mines, Tech. Paper No. 345*, 1-11 (1925). Geology of the coal fields. E. M. SPIEKER. *Ibid* 13-22. Analyses of mine samples. A. C. FIELDNER, H. M. COOPER and F. D. OSGOOD. *Ibid* 23-72. Fusibility of coal ash. *Ibid* 73. Analyses of delivered coal. N. H. SNYDER. *Ibid* 74-7. Low-temperature coking of Utah coals. A. C. FIELDNER. *Ibid* 78-85. E. H.

Researches on some constituents of lignites. III. R. CIUSA AND A. GALIZZI. *Ann. chim. applicata* 15, 209-14(1925). — It has already been shown (cf. C. A. 15, 2708) that 2 hydrocarbons  $C_{15}H_{28}$  (I) and  $C_{15}H_{26}$  (II) besides simonellite are present in Fognano lignite. The work was continued by extg. the lignite with  $Et_2O$  and washing the ext. with 10%  $HCl$ , which gave a soln. contg. basic compds., and then with 10%  $NaOH$ , which gave a soln. contg. phenols and acids. Expts. are to be described later on these solns., the present work being confined to the residual  $Et_2O$ -sol. neutral oil. After evapn. of the  $Et_2O$  and washing with  $H_2O$  the thick brown oil was boiled with  $Na$  and the residual tar was fractionally distd. *in vacuo*. After crystn. of the simonellite from the higher fractions, the mother liquor and other fractions were fractionated separately over  $Na$  *in vacuo*, giving 3 hydrocarbons, all optically active, and having the compns. I, II and  $C_{17}H_{34}$  (III), the last not having been isolated in the previous work. Br-absorption detns. indicated that both II and III were composed of a mixt. of *satd.* and *unsatd.* isomers, the latter being decompd. by  $Br$  or by  $KMnO_4$ . Distn. of II in an  $O$ -free atm. gave an oil with a terpene odor, b.  $230-49^\circ$ . The unsatd. isomer in II reacted

with Br and by fractionation *in vacuo* could be sepd. from its satd. isomer, the latter  $b_{10}$  147°,  $\alpha_D^{20}$  20.46°. Similarly from I a *monobromo deriv.*,  $C_{11}H_{22}Br$ , was obtained,  $b_{11}$  185°. The formula indicated that 2 Br was first absorbed, followed by elimination of HBr. From III a satd. *compd.*  $C_{10}H_{24}$  was obtained,  $b_{10}$  200-11°. On steam distn. the lignite gave a thick, greenish oil with a pinene odor (135 g. from 39 kg.) in which III was absent. Fractional distn. gave the *compd.*  $C_{10}H_{24}$ ,  $b$  140-1°, a *compd.* which was absent in the  $Et_2O$  ext. of the lignite. I, II and III were present in about the same proportions in the  $Et_2O$  ext.

C. C. DAVIS

**Cold-peat.** The new way to open up immense beds of peat. LOUIS GOLDBERG *Warme & Kälte Tech.* 27, 89-91(1925).—G. proposes to divide the beds into sections by water-tight walls, and freeze each section by artificial cold. This will cause the peat to lose its water, which will then be pumped off, the peat being removed as a powder.

ERNEST W. THIELE

**Present status of the gas industry in France.** A. GREBEL. *Technique moderne* 17, 293-8(1925).

A. PAPINEAU-COUTURE

**Sulfur content of illuminating gas.** A. GREBEL. *Chimie et industrie* 13, 911-2(1925).—Brief discussion of the various tests used in testing gas to see if it is up to specifications, and of the importance of the removal of  $CS_2$ .

A. PAPINEAU-COUTURE

**Ammonia plants.** M. BERGER. *Apparatebau* 37, 171-2(1925).—Brief description of the prepn. of  $NH_3$  solns. from gas liquors.

J. H. MOORE

**The operation of (gas) generators with water-cooled shells.** C. MARISCHKA. *Gas u. Wasserfach* 68, 405(1925).—The  $H_2O$  temp. should be maintained well above 100° to prevent condensation on the inner wall of the shell, if the temp. be kept down to 60° to reduce deposition of solids from the  $H_2O$  the corrosion of the inner wall will cause failure within 2 years. It is evident that the thermal efficiency is also higher, since when cooling to a  $H_2O$  temp. of 60° only a small part of the heat removed can be recovered by use of the hot  $H_2O$  as boiler feed as the vol. which must be put through the shell far exceeds boiler requirements.

WM. B. PLUMMER

**Use of Rashing rings with rotary gas washers.** K. H. RAUFF. *Gas u. Wasserfach* 68, 438-9(1925).—Fe rings 25 mm. outside diam., 25 mm. high and of 0.8 mm. sheet after a year's continuous service in standard  $C_2H_4$  and  $NH_3$  rotary washers showed no loss in wt. and did not tend to clog up as did the wooden fillers previously in use.

WM. B. PLUMMER

**The behavior of brown-coal briquets in gas producers.** H. TRUTNOVSKY. *Braunkohle* 24, 373-8(1925).—The resistivity of briquets to disintegration under conditions existing in the producer was tested by coking  $40 \times 31.5 \times 20$ -mm. briquets in an Fe lab. retort and detg. the compressive strength of the resultant coke. The  $H_2O$  content, particle size, % ash, tar yield, or ultimate analysis does not give a satisfactory basis for explaining the observed differences. For briquets from a given coal decreasing the %  $H_2O$  29-11% decreased the compressive strength 11-4 kg./sq. cm., while drying completely caused the briquet to crumble on coking; from a comparison of 2 different coals, however, the one with the lower %  $H_2O$  had the greater strength. The bitumen content (% sol. in  $C_6H_6$ -alc.) apparently gives a usable basis for comparison, the variation therein corresponding in all cases to the observed differences in strength. In a given series prepd. by complete extn. of the coal and final addn. of the desired amt. of bitumen, increasing the % bitumen 0-20% decreased the strength 8.5-2.8 kg./sq. cm. The character of the bitumen is a factor whose influence is perceptible but not yet detd.

WM. B. PLUMMER

**The ultimate analysis of fuels and flue gas.** A. B. HGLBIG. *Chem.-Ztg.* 49, 485-8(1925).—The heat liberated in a given combustion process is equal to  $A \cdot B - C$ , where  $A$  is the amt. of flue gas per unit of fuel as calcd. from the O balance,  $B$  the total heat of formation of the  $CO$ ,  $CO_2$ , and  $H_2O$  present in the flue gas, and  $C$  the heat of formation of the fuel,  $C$  is calcd. as  $8080 C + 28700 H + 2220 S - W$ , where  $C$ ,  $H$ , and  $S$  refer to their % in the fuel and  $W$  is the heat of combustion of the fuel as calorimetrically detd. The detn. of the hydrocarbon constituents of the gas in order to det. the heat liberated is avoided by the use of the term  $C$  above.

WM. B. PLUMMER

**The determination of unburned gases in flue gases.** PAUL NETTMANN. *Warme & Kälte Tech.* 27, 119-21(1925).—For a certain time the flue gases are drawn through heated  $CuO$  and then through any suitable  $CO_2$  recorder. By a suitable automatic valve mechanism the connections are changed so that the gases pass directly to the recorder, while the  $CuO$  is revived by drawing air through it. The  $CuO$  may be heated by the furnace itself.

ERNEST W. THIELE

**Combustion calculations and flue-gas diagram.** WILHELM GUML. *Feuerungs-*

technik 13, 195(1925)—In boiler calcns. it is difficult to det. the unburned C directly, and it is better to calc. it from the flue gas and fuel analyses by the method of Helbig (C. A. 16, 634).

ERNEST W. THIELE

The analysis of combustion gases in industrial furnaces. E. MONTRICHARD. *Rev. gen. elec.* 16, 743-8(1924); *Science Abstracts* 28B, 117-8—The principles of the analyses of the flue gases from coal furnaces are considered with a view to obtaining economy in fuel for the purpose of reducing the cost of production in factories. To make the best use of fuel it is necessary to keep a check on the rate of vaporization, on the unburnt quantity in ash and clinker, and on the temp. of the gases and their CO<sub>2</sub> content. The irregularity of feeding and the necessity for proportioning the speed of combustion to the needs of the moment do not permit solely of the draft being regulated, nor do they allow a fixed thickness of fire to be detd. for perfect combustion. It is important to obtain the max. CO<sub>2</sub> content with the min. of excess air. Some data referring to the combustion of coal are given. Heat loss in the flue gases is given approx. by the following:  $Q = (0.6C/CO_2 + 0.5[9H + E]/100)T$ , where C = % of coal, CO<sub>2</sub> = % of carbon dioxide, H = % of hydrogen, E = % water in the coal, and T = temp. difference between the gases and external atm. The properties required by a suitable app. for flue-gas analysis are accuracy of indicating the result, ease of manipulation, and maintenance. The operations of extn. and analysis should depend on nothing but purely mech. movements, so that they do not vary with different operators. Some types of flue-gas analyzers are described with illustrations.

H. G.

The Schoop process in combustion technology. E. BELANI. *Feuerungstechnik* 13, 232-4(1925)—B. describes the Schoop metal-spraying process and suggests its application to the protection with Al or Cu of grates, boiler tubes, oil stills, low-temp. coke ovens, etc.

ERNEST W. THIELE

The combustion of carbon. II. F. G. KEENEN, L. W. PRINE and W. C. EBAUGH. *Ind. Eng. Chem.* 17, 804-5(1925); cf. Smith and Ebaugh, C. A. 19, 2553—C electrodes, maintained at incandescence by varying currents, were treated with O in suitable quartz app. and the products of combustion analyzed. With high amperages, and therefore high temps., a relatively poor contact of O with C for very short periods of time—say 1/10th of a sec.—enables it to appear as CO rather than CO<sub>2</sub>. The depth of a fuel bed required to yield CO will, therefore, be detd. largely by the temp. that can be maintained and by the intimacy of contact with O. This depth is probably much less than generally supposed.

W. C. EBAUGH

Combustion in the gasoline engine. C. C. MINTER. *Ind. Eng. Chem.* 17, 687-90 (1925).—Exhaust gas from an engine running on a block was drawn through one cell of a thermal-cond. app. of the diffusion type, air filling the second cell. After a reading of the galvanometer was made, the percentage of CO<sub>2</sub> was detd. in an Orsat app. If the reading of the galvanometer had not changed, the reading was recorded. In this way a large no. of readings were obtained when the engine was operated under widely varying conditions. The straight-line plot shown for the data (galvanometer deflection vs. percentage of CO<sub>2</sub>) proves the constancy of the proportionality between H<sub>2</sub> and CO<sub>2</sub> throughout the range 8-14% of CO<sub>2</sub>. The relation (according to Fieldner and Jones, C. A. 15, 594) is as follows: H<sub>2</sub> = 8-0.556 CO<sub>2</sub>. The results of M. confirm this equation. The water-gas equil. exists in the cylinder and equil. is obtained. The same proportionality for CO<sub>2</sub> and H<sub>2</sub> is found in the Bunsen flame, but since the hydrocarbons burned were different, the graphs do not coincide. By operating the engine on city gas, M. hopes to calc. the water-gas equil. const., and thereby det. the max. temp. of the combustion. At the same time, the data would prove whether or not equil. is reached in the Bunsen flame. Incomplete volatilization of a motor fuel should give different max. temps. of combustion and therefore different percentages of CO<sub>2</sub> for the same fuel-air ratio. It is, therefore, not satisfactory to det. CO<sub>2</sub> alone. The thermal-cond. app. as used by M. proves the simultaneous disappearance of CO<sub>2</sub> and H<sub>2</sub> under these conditions, and therefore gives an indication of the fuel-air ratio and qualitatively of the degree of compression and max. temp. of combustion.

W. F. FARAGHER

Some aspects of oxygen enrichment of combustion air in heating-furnace practice. W. C. BUELL, JR. *Proc. Eng. Soc. Western Pennsylvania* 41, 133-55(1925).—A study of the theoretical, economic and operating factors encountered when free O<sub>2</sub> is added to the air and fuel used in industrial furnaces. Pittsburgh natural gas is considered. Conditions of enrichment, partial combustion data, effect of enrichment, the thermal capacity of products of combustion, and the O<sub>2</sub> requirements in continuous furnace operation are tabulated. The relation between preheat and flame temp. under different conditions of enrichment is indicated. Possible advantages claimed for enrichment include: saving of capital charges and upkeep cost of preheat equipment, and smaller

furnace structure in cross-section; and bridge walls, ports and other designs for mixing are absent. Smaller cross-sectional areas permit closer contact between the products of combustion and the metal with attendant more efficient heat transfer. A lengthy discussion is included. W. H. BOYNTON

**Tipping and turning grates.** BENEDICT. *Feuerungstechnik* 13, 223-4(1925).—Two types of hand-fired grates are illustrated in which part of the grate may be tipped or turned aside by the fireman while cleaning, leaving a gap into which the ash may be easily shoved. ERNEST W. THIELE

**The influence of rotary retort construction on the composition of primary tar and light oils.** F. MÜLLER. *Brennstoff-Chem* 6, 125(1925); cf. *C. A.* 19, 719.—M. replies to the criticism of the double rotary retort by Hoffmann (*C. A.* 6, 719, 720) who believes this construction promotes decompn. of tar and light oils. The double oven is provided with means of admitting steam at the point where intensive carbonization takes place, furthermore tests of the oven have shown that the gas yield does not run over 70 cu. meters per ton which yield indicates primary carbonization. J. D. DAVIS

**The influence of rotary retort construction on the composition of primary tar and light oils.** FRITZ G. HOFFMANN. *Brennstoff-Chem.* 6, 145(1925); cf. preceding abstr. and *C. A.* 19, 720.—H. thinks the fact that there is not excessive decompn. of tars in the double rotary retort is due to the admission of sufficient steam and not to the retort design. A single rotary would give good results in steam. J. D. DAVIS

**Formula weights of low-temperature phenols.** J. J. MORGAN AND M. H. MEIGHAN. *Ind Eng Chem* 17, 854-6(1925).—The mol. wt. and sp. gr. of the phenols from 2 com. low-temp. tars (Carbocoal and Doherty Hydrogas) are tabulated and plotted vs. their b. p. The latter mixt. of phenols shows higher and lower values, resp., for the above properties than do the Carbocoal tar acids, which indicates the cracking to have been less since high-temp. tar acids are characterized by low mol. wt. and high sp. gr. The mol. wts. have been detd. by the Na method of M. and M. (cf. *C. A.* 19, 2267). WM. B. PLUMMER

**Preparation of dense low-temperature coke without the use of pressure.** W. KRÖNIG. *Brennstoff-Chem* 6, 133-8(1925).—Expts. were made which showed the effect of mixing semi-coke with coal to be coked on the density of the product. Coke densities were detd. by the sand-displacement method. Mixts. were coked in a 20-g. cast Al retort, the following conditions being varied: grain size of both coal and semi-coke; rate of heating; proportion, coal to semi-coke; density of semi-coke used. Conclusions: For swelling coals the density of the coke obtained increases with fineness of the coal. The optimum size for semi-coke used for mixing is 0.137-0.085 mm. There is an optimum heating rate, which varies with the swelling tendency of the coal; heating rates must be slow for strongly swelling coals. For each coal there is an optimum amt. of admixed semi-coke required; the best results were obtained with mixts. around 1:1. The suitability of semi-coke for mixing depends much more on its absorptive capacity than on its density. Non-coking coals can be substituted for semi-coke in the mixt. to make a denser coke than can be made by the coal alone. It is possible to make a low-temp. coke of density 0.7 to 0.9 by mixing a suitable amt. of semi-coke with the coal to be coked. J. D. DAVIS

**Refractories and coke-oven technology.** G. E. JUNIUS. *Brennstoff-Chem* 6, 139-143(1925).—Recent increase in the capacity of coke oven with reduction of coking time has called for the development of better refractories. Pure fire clay (46% base and 54% acid) m. 1700°, but the usual impurities in com. clay lower its m. p. to about 1580°. Furthermore pure clay is subject to shrinkage in oven walls causing cracks. The Otto Company formerly used a conglomerate from Dalhausen which analyzed 90-93% SiO<sub>2</sub> and melted at about 1700°. This material does not shrink. Attempts to use highly refractory clays have failed because although the actual m. p. of clay is high, its softening point under load is low. Of a clay and a silica, both m. 1700°, the former will soften at 1350 and the latter at 1600° under a load of 1 kg. per sq. cm. Successful use of silica refractories made from quartzite in American has led to German development of this material. The Otto Co. now uses a silica refractory made by mixing ground quartzite with milk of lime (2%), drying and burning at 1450-1500°. Care should be used in selecting the quartzite, particularly as regards its mineral impurities; feldspar is to be avoided since it m. 1200°. The minerals present can best be distinguished by microscopic exam.; illustrations are given. Grain size of quartz is of importance since large grains require longer burning. Well-burned silica refractories will have the following expansion coeffs.: at 15 to 300°,  $3.75 \times 10^{-7}$ ; at 300 to 500°,  $100 \times 10^{-7}$ ; at 500 to 600°,  $83 \times 10^{-7}$ ; at 600 to 750°,  $55 \times 10^{-7}$ . One can calc. the expansion of an oven battery at 15%. Properly made silica refractories are the best obtainable for oven

construction; experience has shown that ovens built of this material withstand placing in and out of operation particularly well  
J. D. DAVIS

Oil obtained by hydrogenation of semi-coke by the Bergius method. H. TROTSCH AND W. TER-NEDDEN. *Brennstoff-Chem.* 6, 143-5 (1925) —Semi-coke from brown coal (cf. C. A. 19, 1768), was heated with H in an autoclave for 16 hrs. at 460° and 200 to 260 atm and the oil formed was directly distd. from the autoclave. The oil after sepn. of 27% water yielded 46% b 65-280°, 14% viscous oil distg. with superheated steam and 13% asphalt-like pitch. From the oil b 280°, 22% tar acids were sepd. by shaking with 3 N NaOH. These were fractionally distd. and yielded phenol 23, o-cresol 11 and m-cresol 14%. p-cresol was not found. m-xyleneol amounted to 20% of the fraction b 210-215°. After sepn. of the bases (3.5%) by shaking with 5 N H<sub>2</sub>SO<sub>4</sub>, the neutral oils were examd. and found to consist largely of satd. cyclic hydrocarbons. Unsatd. hydrocarbons amounted to only 10% of the neutral oil  
J. D. D.

The recovery of pitch, tar oils, ammonia, and hydrogen sulfide from coke-oven gas by the Feld process. W. FUNKE. *Gas u. Wasserfach.* 68, 388-90, 402-5, 417-20, 433-5 (1925) —The construction and operation of 2 com.-scale plants are described in detail. The gas is successively washed to remove tar fractions, NH<sub>3</sub> and H<sub>2</sub>S, and finally the lighter oils; the following list of washings gives the fraction removed, the washing agent, and the working temp.: pitch, liquid pitch, 160°; heavy tar, tar, 130°; heavy oil, heavy oil, 100°; NH<sub>3</sub> and H<sub>2</sub>S, polythionate liquor, 80°; middle oil, water, 30°; light oil, middle oil, 18°. The polythionate liquor contains mainly NH<sub>4</sub> tri- and tetra-thionate, and is originally prepd. from NH<sub>3</sub>, S, and SO<sub>2</sub>; in use the NH<sub>3</sub> and H<sub>2</sub>S are absorbed from the gas with formation of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>3</sub>, and S, the latter 2 substances being sepd., the former reconverted into polythionate by means of SO<sub>2</sub>. The (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> as sepd. from the polythionate wash liquor was of good purity and low acidity but turned red on standing because of presence of NH<sub>4</sub>CNS. At one of the 2 plants the H<sub>2</sub>S was present in the gas in excess of a 1/2 ratio to the NH<sub>3</sub>, and the removal of both from the gas was nearly complete; at the other plant the H<sub>2</sub>S lacked 39% of reaching the equiv. 1/2 ratio and only 30% of the S was removed from the gas; the polythionate wash liquor always contained free NH<sub>3</sub>, the trouble apparently being due to the high concn. of CO<sub>2</sub> also present in the gas.  
WM. B. PLUMMER

Determination of oxides of N (except N<sub>2</sub>O) in small concentration in the products of combustion of coal gas and air (FRANCIS, PARSONS) 7.

Liquid hydrocarbon fuel. A. N. KERR. U. S. 1,545,261, July 7. A liquid fuel adapted for domestic use comprises a cut of natural gas condensate having an initial b. p. not lower than about -12°, a final b. p. not higher than about 65°, a d. of 91-120° Bè. and a vapor tension of 15-20 lbs. at 22°.

Carbonaceous fuel (residue from oil cracking). G. EGLOFF and H. P. BENNER. U. S. 1,543,833, June 30. A pitchy C residue is treated with pressure distillate produced by oil cracking to free it from its oily constituents for use as a fuel. Cf. C. A. 19, 393.

Fuel for portable vulcanizers. R. H. CHURCHILL. Brit. 227,717, June 13, 1924. A granular mixt. of pulverized Al and S is mixed with finely divided Pb, with or without Fe as a retarding agent.

Carbonizing coal, etc., and reducing ores. H. NIELSEN and B. LAING. Brit. 227,880, Aug. 17, 1923. In distg. coal, sewage, etc., or in reducing Fe ore or other ores, the powd. material is fed into one end of a rotary retort and carried forward in contact with hot gases from combustion of powd. fuel. Air, and if desired steam also, is introduced into the interior of the retort at one or more points along its length.

Dewatering peat. K. MAUS. Brit. 227,673, March 27, 1924. Mech. features of pressing, etc.

Combustion regulation. G. H. GIBSON. U. S. 1,544,310, June 30. Combustion in boiler furnaces is automatically regulated in accord with the rate at which H<sub>2</sub>O is supplied to the boiler and steam withdrawn from it.

Gas from coal, etc. E. R. SURCLIFFE. Brit. 227,879, July 25, 1923. In the distn. of coal or similar materials, superheated steam is passed through hot fuel to obtain a combustible gas which is used in part to heat the charge and in part to heat one of a plurality of superheaters that are alternately used for heating the steam before admission to the charge. Working temps. of 750-1200° are used according to the products desired. An app. is described.

Gas manufacture. J. RUDÉ. Brit. 227,726, June 27, 1924. A modification of Brit. 218,925 (C. A. 19, 573).

Gas purifier. H. LUMB, J. E. HORSEFALL and R. DEMPSTER & SONS, LTD. Brit. 227,623, Jan. 10, 1924. Gas may be passed in either direction through the purifier.  
 Gas producer. G. H. BENTLEY and E. G. APPELEY. Brit. 227,346, May 22, 1924.  
 Charging coke ovens. J. SCHAEFER and COLLIN & CO. Brit. 227,470, Jan. 12, 1924. The fuel is delivered with such velocity that the charge is compressed into a dense cake.

## 22—PETROLEUM, LUBRICANTS, ASPHALT AND WOOD PRODUCTS

F. M. ROGERS

The physical chemistry of oil-field emulsions. D. B. DOW and C. E. REISTLE, JR. Bur. Mines, *Repts., Investigations* No. 2692, 14 pp (1925).—Properties of clear oil were compared with those of oil sepd. from the emulsion of cut-oils by heating in a pressure bomb at temp. well below the cracking range. The ash of the water-free recovered oil was in one case 2.6%, while that of the clear oil (sepd. from the emulsion and the water by centrifuging the cut-oil) was 1.2%. The A. P. I. gravity of the oil from the emulsion is usually lower than that of the clear oil, while the viscosity is higher, and the vol. of the lubricating distillate (Bur. of Mines method) is larger. The carbon-residue test is usually higher for the oil from the emulsion, also. Asphalt was extd. by mixing the residual oil (Bur. of Mines distn.) with sand, and extg. first with acetone and then with  $C_2H_2$ . As a rule, the asphalt was higher in the oil from the emulsion than in the clear oil. Both the oil and asphalt acted as emulsifying agents when added to kerosene and water. The theory of emulsions and the bearing of it on cut-oils are discussed.

W. F. FARAGHER

Oils distilled from the bituminous schists of Castoreale and Barcellona (Sicily). MARIO GIORDANI *Ann. chim. applicata* 15, 214-26 (1925).—Distn. of the schists of Castoreale and Barcellona gave a clear, red brown oil, d. 0.970,  $n_D^{20}$  1.532, viscosity at 15° 52.4 (Redwood), av. mol. wt. 127, I no. 113.9 and S. 3.2%, with yields varying from 8 to 15%. Distn. of the oil to dryness, purification of the distillate with  $H_2SO_4$  and NaOH and fractionation of the purified oil gave in %: naphtha 2, illuminating oil 6, heavy oil 15, lubricating oil 15, paraffin 13. The low % naphtha was due to the method of distn. On fractionation of the oil, the successive fractions increased in d, in the values of  $n$  and in the av. mol. wt., while the I no. decreased. There was no definite relation either between the I no. or between the av. mol. wt. and the state of unsatn., for the latter was lower than that calcd. from the I no. and higher than that calcd. from the mol. wt. Distn. therefore, at least in a current of steam, caused a slight decompn., which in general is difficult to avoid with oils rich in unsatd. compds. Treatment of the oil with  $H_2SO_4$  gave an unattacked residue of 16.7%, with  $HNO_3$  (cf. Marcusson, *C. A.* 5, 3728) indicated that about 15% consisted of aromatic hydrocarbons and with  $H_2SO_4 + HCHO$  (cf. Marcusson, *loc. cit.*) gave an av. formolite no. of 105.3, one of the highest formolite nos. ever reported. The latter in conjunction with the  $H_2SO_4$  reaction made it probable that the unsatd. constituents were almost wholly cycloid hydrocarbons. Distn. of the oil by the method of Franks, except that steam distn. was employed, indicated that even with steam extensive decompn. occurs with such oils, with a decrease both of unsatd. compds. and of S in the successive distns. Since oil distillates from bituminous schists are inferior to petroleum products chiefly because of high amt. of S and of unsatd. compds.; this method of distn. offers a means of increasing the value of schist oils by reducing the S and the unsatd. compds. to practicable limits.

C. C. DAVIS

The desulfuration of petroleum oils. E. H. LOZANO. *Quim. e ind.* 2, 92 (1925).—Good results were obtained with concd.  $HNO_3$ . Org. S was converted into  $SO_2$ , asphalt and higher aromatic compds. were pptd. By subsequent treatment with alkali and Mg or Zn the excess  $SO_2$  is neutralized, the  $NO_2$  compds. reduced and the resins dissolved.

MARY JACOBSEN

A test for relative decolorizing efficiencies of clays. J. B. HILL, L. W. NICHOLS and H. C. COWLES, JR. *Ind. Eng. Chem.* 17, 818-9 (1925).—Four g. of burned clay is placed in an 8-oz. bottle with 100 cc. of a standard methylene blue soln. at 32.2° = 1.67° and shaken for 10 min. at a rate of 100-200 shakes per min. The standard soln. is made by dissolving 0.25 g. of methylene blue in 0.1 N  $H_2SO_4$  and making the vol. to 1 l. The soln. is adjusted so that when dild. with 9 vol. of  $H_2O$  in a 4-oz. oil-sample bottle, the color matches a standard soln. of  $CoCl_2$  in a similar container. The  $CoCl_2$  soln. is

made by dissolving the salt in a mixt. of 95% alc. (97.5% by vol.) and 32% HCl (2.5% by vol.). At 15.6°, there is 0.4700 g. of  $\text{CoCl}_2$  per 100 cc. of soln. Color standards for comparison are made from the standard soln. by diln. with  $\text{H}_2\text{O}$ , and are marked with numbers showing the vol. percentage of the original standard in each. The soln. is poured from the burned clay after shaking, and is centrifuged before comparison with the numbered solns. Comparisons of *methylene blue numbers* with percolation tests on oils are presented. The method is suitable only for burned clays. W. F. FARAGHER

**Tetraethyl lead poison hazards.** T. MINGLEY, JR. *Ind. Eng. Chem.* 17, 827-8 (1925).—Hazards in manuf., handling and mixing with gasoline, distribution of treated gasoline, and using of treated gasoline are discussed. The advantage to the public attendant upon the use of  $\text{PbEt}_4$  in gasoline are such that "unless a grave and unescapable hazard exists in the manuf. of  $\text{PbEt}_4$ , its abandonment cannot be justified." Serious hazards are limited to manuf. and handling of  $\text{PbEt}_4$  itself; these hazards are recognized and can be controlled.  $\text{PbEt}_4$  is a slow poison, 0.05 as poisonous as  $\text{HgCl}_2$ . The *symptoms of poisoning* are, in order of appearance, drop of blood pressure, drop of body temp., reduced pulse-rate, sleeplessness, loss of wt., nausea or tremor, and delirium tremens. In early stages, removal from exposure gives complete restoration. If sleeplessness has developed, the patient is kept in the open air and given light exercise, without use of soporifics. W. F. FARAGHER

**Measurements of friction with lubrication.** PAUL WOOD. *Compt. rend.* 180, 1824-6(1925).—Friction measurements are made on a series of oils with a slowly rotating disk on which a brake is applied. A lever records the applied pressure automatically. Surfaces of soft steel and hard Ca are used and a special technic is applied to obtain comparable results. Above room temp. the lubrication decreased in all cases with increasing temp., except when fatty acids were present, where the decrease started at higher temps. J. T. STERN

**Some observations on the colloidal character of asphalts.** R. E. KIRK AND L. H. REYERSON. *J. Phys. Chem.* 29, 865-71(1925).—"CuSO<sub>4</sub> acts on the mineral matter present in Trinidad asphalt, increasing the number and decreasing the apparent size of the colloidal particles. The change involves the mineral matter present as well as an action between the bitumen and the CuSO<sub>4</sub>. The dispersion of asphalts in org. liquids involves both the dispersion of inorg. matter and possible dispersion of some of the org. matter present." F. L. BROWNE

**Protection of oil- and gas-field equipment against corrosion (MILLS) 9.** Oil obtained by hydrogenation of semi-coke (TROTSCH, TER-NEDDEN) 21. Reclaiming cotton from oily wastes (Brit. pat. 227,253) 25. Carbonaceous fuel [residue from oil cracking] (U. S. pat. 1,543,833) 21.

MCKEE, RALPH H., ELLS, S. C., GAVIN, M. J., GEORGE, R. D., GOODWIN, R. T., HAMOR, W. A., KARRICK, L. C., and LYDER, E. E. *Shale Oil*. Am. Chem. Soc. Monograph. New York: Chemical Catalog Co., Inc. 326 pp. \$4.50. Reviewed in *Ind. Eng. Chem.* 17, 876(1925).

**Blended gasoline.** H. COONEY. U. S. 1,543,750, June 30. Details of fractional condensation of gasoline from natural gas by successive stages of compression and cooling, and of heat-interchange and mixing with a straight-run gasoline. An app. is described.

**Removing asphaltic and ozocerite-like substances from hydrocarbon mixtures.** H. NEUMANN. U. S. 1,545,440, July 7. Hydrocarbon mixts. such as crude East-Galician or Boryslaw oil are heated and mixed with  $\text{H}_2\text{O}$  contg. trivalent Fe and halogen ions, e. g., derived from the addn. of  $\text{FeCl}_3$ , the mixt. is allowed to settle to form an oily and an aq. layer and the oily layer is cooled to sep. solid ozocerite-like hydrocarbons.

**Purifying oils.** P. W. PRUTZMAN and C. J. VON BIERA. *Brit.* 227,177, Oct. 8, 1923. See U. S. 1,471,201 (C. A. 18, 166).

**Apparatus for electrical dehydration of petroleum oils.** R. E. LAND. U. S. 1,543,928, June 30. The app. has rotating electrodes with stationary electrodes between them.

**Apparatus for converting hydrocarbon oils.** C. P. DUBBS. U. S. 1,543,831, June 30. Heating and vaporizing coils (the latter of larger diam.) each have a pump for maintaining a local circulation of oil within them.

Converting heavy hydrocarbons into lighter products. C. P. DUBBS U. S. 1,543,832, June 30 A small stream of oil is passed through a heating zone and discharged into a distg zone of larger cross section with an independent local pump circulation (as in the app of U S 1,543,831, above), these circulations taking place at substantially the same level and in a substantially horizontal plane. Pressure is maintained during the distn of the oil Cf C. A. 19, 1773

Apparatus for reclaiming gasoline used for cleaning purposes. A. D. STEWART. U. S. 1,545,210, July 7.

Separating wax from mineral oils. L. D. FULTON. U. S. 1,544,734, July 7 A large vol of mineral oil contg wax in soln is caused to flow slowly along a downward path without agitation and without substantial change of direction, and after indirect counter-current cooling is subjected to centrifugal sepn

Purifying lubricating oils. J. DREYFUS Brit. 228,162, Jan 24, 1924. Lubricating oil from internal combustion engines is purified by treatment with a mixt. contg adsorbent material such as fuller's earth or pulverized firebrick and salts of acids "of high valency" such as K and Al sulfates or other sulfates, phosphates, tellurates, selenates, antimonates or arsenates

Separating wax from lubricating oils. C. H. HARGOOD. U. S. 1,544,747, July 7. The wax-bearing oil flows continuously through preliminary and final double pipe chillers to a centrifuge. Oil from the latter is used for cooling purposes in the preliminary chiller.

## 23—CELLULOSE AND PAPER

CARLETON E. CURRAN

The action of aqueous sulfurous acid on lignocellulose. II. C. F. CROSS AND A. ENGELSTAD *J. Soc. Chem. Ind* 44, 267-70T (1925) —In previous work (cf. C. A. 18, 3054) C and E. have shown that cooking of spruce wood with 7-8%  $\text{SO}_2$  solns at temps. of 90-110° leads to a sepn of the wood into fibers but delignification is not complete, the pulp being harsh and unbleachable. Addn of 0.1 to 0.5%  $\text{NH}_3$  to the  $\text{SO}_2$  solns results in complete cooking of the wood. Addn of other bases such as Na, Ca and Mg, as in ordinary bisulfite process, permits the use of lower  $\text{SO}_2$  concn but necessitates higher cooking temp. Cooks were made at 90-110° for 24 hrs. with acid solns of 7-8%  $\text{SO}_2$  and 0.25%  $\text{NH}_3$ , and equiv. quantities of Na, Ca and Mg. The acid contg  $\text{NH}_3$  gave a greater degree of cooking with a much lower yield of uncooked chips. With a  $\text{SO}_2$  concn of only 5%, similar to that used in the ordinary bisulfite process, but with all other conditions the same as before, the acid contg.  $\text{NH}_3$  again showed a greater reduction in undercooked chips. Expts. were made with  $\text{PhNH}_2$  and  $\text{PhNHNH}_2$  in concns equiv. to 0.25%  $\text{NH}_3$ . In both cases no cooking took place. These expts bring out the sp. reactivity of  $\text{NH}_3$  with the CO group of the lignin complex. It appears to add to the CO group forming a hydrated mol compd. while  $\text{PhNH}_2$  and  $\text{PhNHNH}_2$  give full reactions with elimination of  $\text{H}_2\text{O}$ , rendering the CO group incapable of further reaction. Com. cooks with  $\text{SO}_2$  solns. contg.  $\text{NH}_3$  bear out the exptl results. It is concluded that in the ordinary bisulfite process the sulfonation of the lignin proceeds by addn. of the bisulfite to CO groups, followed by rearrangement and addn. to the double bond in the acrylic side chain of the lignin complex. The excess  $\text{SO}_2$  present serves in a hydrolytic and decolorant capacity. In the  $\text{H}_2\text{SO}_3$  process the acid alone is more reactive than bisulfite, the sulfonation proceeding at lower temps and going to completion when small concns of  $\text{NH}_3$  are present. In addn. to the advantage gained by use of lower temp., the factor of elimination of basic materials is avoided if the liquor from the cooks is to be further utilized. W. H. SWANSON

The lignosulfonic acid obtained from spruce wood by the action of sulfurous acid in the presence of ammonia. CHARLES DORGE AND LESLIE HALL. *J. Soc. Chem. Ind* 44, 270-47T (1925); cf. C. A. 18, 3054 —The liquor obtained from cooks on spruce wood made with  $\text{H}_2\text{SO}_3$  solns. contg. 0.1 to 0.5%  $\text{NH}_3$  had a  $\text{H}_2\text{SO}_3$  concn of 0.4% as compared with 4.0% when  $\text{H}_2\text{SO}_3$  was used alone. The sulfonic deriv. isolated after dialysis of the liquor gave a S. N ratio of 2:1, corresponding in compn. to a mono- $\text{NH}_2$  salt of the acid  $\text{C}_6\text{H}_4\text{O}_3\text{N}_2\text{H}_4\text{SO}_3$ , a formula suggested by Klason for a lignosulfonic acid. The N was easily removed by alkalis and was probably not combined in a heterocyclic ring. Condensation products with  $\text{PhNH}_2$ , o-toluidine, and  $\beta\text{-C}_6\text{H}_4\text{NH}_2$  indicated them to be sp. to the lignosulfonic acid and did not fractionate it into  $\alpha$  and  $\beta$  modifications, but served to sepn the lignin as a whole from the rest of the wood com-

ponents Basic lead acetate fractionated the liquor by giving an insol. lead lignosulfonate ppt. first. The filtrate when treated with alc gave a ppt. of a lead compd. of a sulfonated hemicellulose. The filtrate from this contained carbohydrates, among which mannose was identified. The lignosulfonic acid gave condensation products with phenol. In the case of gallic acid an ink of the ferrugallie type was produced. W. H. S.

The lignin content of pine wood. A. C. v EULER *Svensk Pappers-Tid.* 28, 52-6(1925).—E gives further data to show that Klason's criticisms (cf. C. A. 17, 3788) of E.'s original paper (cf. C. A. 17, 2049) were erroneous. W. SEGERBLÖM

Indicators for the cellulose industry. E. ÖMAN. *Svensk Pappers-Tid.* 28, 234-6, 274-6(1925).—In detg free  $\text{SO}_2$  bromophenol blue is superior to Me orange because the uncertain range at the change of color is about one fourth as great. Titration with bromophenol blue also reduces the error in the Ca no. from  $\approx 5\%$  to  $\approx 1\%$ . *p*-Nitrophenol is unsatisfactory. The indicators falling within the range  $p_H \approx 9.3$  are: phenolphthalein, colorless, 8.2-10.0, red; thymol blue, yellow, 8.2-9.5, blue; thymolphthalein, colorless, 9.3-10.5, blue. The first is least satisfactory; the last is the best. Phenol red and cresol red are not as good as bromothymol blue. The indicators for the three stages in the analysis of white liquors are (1) Porrier's blue, Nile blue (sulfate) and methyl blue, (2) thymolphthalein, thymol blue and phenolphthalein and (3) bromophenol blue and Me orange. Data are given for trials of these with known solns. W. SEGERBLÖM

Ionic reactions in the sulfite-digesting process. E. ÖMAN. *Svensk Pappers-Tid.* 28, 81-4, 106-10(1925).—The dissociation of chemicals taking part in sulfite cooking is shown by reversible equations  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{O}$ ,  $\text{NaHSO}_4$ ,  $\text{Ca}(\text{HSO}_4)_2$ ,  $\text{ROH}$ ,  $\text{RSO}_3\text{H}$ ,  $\text{RSO}_3\text{Ca}$ ,  $\text{Ca}(\text{OAc})_2$  and  $\text{HOAc}$ . The part taken by each in cooking is discussed, with particular reference to the pptn. of Ca. Weak sulfonic acids cannot combine with Ca or neutralize lime in the presence of bisulfite, but remain as free acids. The Ca in the sulfite liquor acts as a buffer to keep down the H-ion concn. and the latter has a great influence on the digesting process and on the pptn. of  $\text{CaSO}_4$ . W. S.

Chemistry of the sulfite process. Acid hydrolysis of wood. R. N. MILLER AND W. H. SWANSON. *Ind. Eng. Chem.* 17, 843-7(1925); cf. C. A. 19, 173.—Powd. spruce wood (after extn. with a mixt. of  $\text{EtOH}$  and  $\text{C}_6\text{H}_6$ ) was subjected to hydrolysis at  $96^\circ$  for 6 hr. by means of  $\text{HCl}$  of concn. varying between 0.05 and 3.00%. The cellulose, based on wood, in the residue (58.88% in wood) was diminished to 51.18, 48.31 and 48.70% by the use of 3.00, 0.75 and 0.05%  $\text{HCl}$ , resp. The reducing sugars formed were estd. and also again after subjection to a further hydrolysis by means of 3.00%  $\text{HCl}$ , 0.75%  $\text{HCl}$  produced 16.15% of reducing sugar on the wood, which was increased to 19.00% by the second hydrolysis; more concd. acid did not increase these quantities materially. A part of the cellulose was hydrolyzed rapidly and the bulk of that part of the wood not classed as cellulose or lignin was hydrolyzed more slowly to sugars; in the more complete hydrolyses nearly all the wood could be accounted for as stable cellulose, lignin and reducing sugars. By repeating the tests, with an aq. soln. of  $\text{SO}_2$  and  $\text{Ca}(\text{HSO}_4)_2$  instead of  $\text{HCl}$ , a similar loss of cellulose was experienced, together with the removal of the lignin. No connection could be observed between the loss of cellulose and lignin, resp. The use of salts of strong acids in addn. to "sulfite acid" appeared to speed up the hydrolysis; salts of weak acids had a contrary effect, suggesting the influence of H-ion concn. FRANCIS G. RAWLING

Effect of presteaming on the hydrolysis of wood. E. C. SHERRARD AND J. O. CLOSS. *Ind. Eng. Chem.* 17, 847-9(1925).—Sawdust in 22-kg. lots was submitted to steaming at pressures between 5.6 and 8.4 kg. per sq. cm. during 5-30 min., followed by hydrolysis with 2.5% by wt. of  $\text{H}_2\text{SO}_4$  on the wood at the same pressure. 125% by wt. of  $\text{H}_2\text{O}$  on the wood was used in each case, half the  $\text{H}_2\text{O}$  being added before the steaming and half with the acid. Presteaming causes little or no increase in the yield of total sugar; fermentable sugars are increased somewhat by longer periods (15 min.) of cooking after the addn. of the acid. The highest yield on the wt. of the wood was 20.93% total reducing sugar, of which 62.79% was fermentable, yielding 5.7% of  $\text{EtOH}$ . F. G. R.

Recovery of caustic soda from esparto and wood pulp boiling liquors. ANON. *Paper Makers' Monthly J.* 63, No. 6, 213-5(1925).—A description of a mech. underfeed stoker for burning the ash from the rotary incinerators used in the esparto and soda wood pulp mills with photographs of the stokers in use at the Carrongrove Paper Co., Ltd. Scotland. FRANCIS G. RAWLING

Selection of pulps in the manufacture of paper. E. ARNOULD. *Rev. univ. papeterie* 7, No. 72, 12-5(Dec., 1924); *Pulp Paper Mag. Can.* 23, 761-2(1925).—A discussion of the properties and selection of the different grades of pulps according to the kind of paper required. Excellent results can be obtained in washing rags directly in the boiler

after cooking by providing the boiler with two rows of teeth about 30-35 cm. long and 40 cm. apart, the function of which is to prevent the rags from gathering together and rolling up into a ball during the boiling and washing. A. PAPINEAU-COUTURE

Carao fiber for paper making. ANON. *Boil. reg. star. sper. indus. caria* No. 2 (1925). *Pulp Paper Mag. Can.* 23, 811-2, 821-2(1925); cf. Shaw and Rumsey, *C. A.* 19, 1032.—Lab. tests indicate that the material in the form of "fite" (decorticated leaves) is suitable for the manu. of textile fiber, and that the waste from the textile industry is suitable as a raw material for paper making. A. PAPINEAU-COUTURE

Micrography of sweet gum pulp. L. VIDAL. *Paper Trade J.* 81, No. 3, 49-50 (1925).—See *C. A.* 19, 2130. A. PAPINEAU-COUTURE

Paper colors and color testing. M. PAVIER. *Paper Trade J.* 81, No. 3, 51-5 (1925).—See *C. A.* 19, 1032. A. PAPINEAU-COUTURE

Disk method of log sampling for moisture test in wood. H. O. KEAY. *Pulp Paper Mag. Can.* 23, 798-7(1925).—Results of moisture tests carried out by the disk method at various points along a number of logs are tabulated and plotted. They indicate in a general way that the moisture content of the log about 6 in. from the end usually is fairly near the av. moisture content of the whole log. A. P.-C.

A contribution to the process of Japanese paper-making. SHIGERU KOMATSU AND GINOSUKE NAKAJIMA. *Mem. Coll. Sci. Kyoto Imp. Univ.* 8A, 257-61(1925).—Analytical data are presented showing the chem. changes of paper, made from young mulberry wood, during the process of manu. W. H. SWANSON

Greaseproof packages. ANON. *Paper Trade J.* 81, No. 2, 32, 34(1925).—Methods of testing are described and results of tests of com. grease-proof papers and boards are given. A study of the grease resistance of silicated board carried out by painting manilla-lined news board with various thicknesses of silicate showed that to render board greaseproof to a useful degree by coating with silicate it is necessary to apply so heavy a coating that the resulting product is unduly thick, can be prepd. only with difficulty, and is too brittle and readily broken to be of practical value. Thinly coated boards, such as have been commonly used, are completely penetrated almost at once. Tests of various samples of dry waxed paper showed them to be of no value whatever as grease-resistant materials. A. PAPINEAU-COUTURE

Paper makers' alum. G. F. KENNEDY. *Paper Trade J.* 81, No. 1, 57-9(1925).—Description of its manu., method of use and specifications. A. PAPINEAU-COUTURE

The bleaching of trade sulfate pulps and cotton with calcium hypochlorite solutions. A. FORSTER AND S. A. PEARMAN. *J. Soc. Chem. Ind.* 44, 233-41T; *Paper Makers' Monthly J.* 63, No. 6, 215-20(1925).—Results of bleaching were measured by the soly. of the product in 3% aq. NaOH and by the lignin value, which was detd. by dissolving 0.1 g. of dried pulp in 25 cc. concd. H<sub>2</sub>SO<sub>4</sub> and comparing the color of the soln. with that obtained from known sulfate pulps. With the use of bleaching powder dissolved in distd. H<sub>2</sub>O, the NaOH soly. of the pulp was raised to 20%, the lignin value fell from 0.64 to 0.24% when 4.54% available Cl had been absorbed by the pulp in 24 hrs. By the use of bleaching soln. made up with lime-H<sub>2</sub>O instead of distd. H<sub>2</sub>O, the NaOH soly. of the pulp was reduced by over 50%, but the lignin value was somewhat higher (0.42%). The use of lime H<sub>2</sub>O bleach liquor effects (1) a great saving in bleach consumed, (2) the production of much less oxycellulose and (3) a slower removal of lignin. Tests extending over 14 days showed that in the absence of lime both cotton and sulfate pulps absorbed as much as 50% of their weight of Cl and were converted into slimes; in the presence of lime, the cotton absorbed only 16.17 and the sulfate pulp 18.9% of Cl, resp., in the same time. By bleaching a sample for 14 days and then boiling it with 3.0% NaOH, the amt. of residue was (1) cotton, no lime 41.1%, with lime 76.1%; (2) sulfate pulp, no lime 28.6%, with lime 70.5%. FRANCIS G. RAWLING

Technical features of high-speed newsprint manufacture. C. W. MORDEN. *Mech. Eng.* 47, 495-6(1925). H. G.

Investigations on the destruction of cellulose by aerobic bacteria. III. Further investigations on the true aerobes and on the denitrification process. J. GROENEWEGE. *Mikrobiol. Abg. Prof. No. Landb. Dtsch. Landb. Nys. Hundel (Dutch East India)* 13, 1-23(1923); *Botan. Abstracts* 14, 172; cf. *C. A.* 15, 2720.—Cellulose is hydrolyzed by the enzyme cellulase to the disaccharide cellobiose, and then by cellobiase to glucose, which is further broken down into acetic, butyric and lactic acids. In neutral or weakly acid media, the cellobiose is so quickly split that little is present at any one time; in alk. media the cellobiose is formed faster than it is split, and a spore-forming flora, particularly varieties of *Bacillus cellobiosus*, hydrolyzes the cellobiose into formic acid, acetic acid and a higher fatty acid, very probably valeric acid. A secondary flora, partly of

spore formers, oxidizes the acids to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Of this secondary flora, the spore formers have not been found to include denitrifiers, while the non-spore formers include both nitrifiers and denitrifiers H. G.

Heat and ventilation in paper plants. K. LINDERSTAM. *Svensk Pappers-Tid.* 28, 133-6, 161-4(1925).—The temp. of fresh and of moist air, the soly. of water vapor in air, and the heat-recovery batteries are discussed. The size of the batteries is detd. by  $G_1 = (V_1 - V_2)/(100 - V_1)$  kg., where  $V_1$  is the % of moisture in the pulp,  $V_2$  is the % of moisture in the finished paper, and  $G$  is the quantity of water which, evapd. from pulp of moisture  $V_1$ , gives 1 kg. of paper with moisture  $V_2$ . Tables of numerical data, and curves drawn therefrom, are given for: (1) the quantity of water necessary to evap. from pulp of varying moisture content to make 1 kg. paper of 10% moisture, (2) quantity of water which 1 kg. dry air can hold in soln., (3) quantities of fresh air and of dry air which can hold 1 kg. water or steam at varying temps. of dry fresh and of moist air, (4) quantities of heat necessary for that amt. of air which holds 1 kg. moisture at different temps., (5) heat surface in the batteries necessary to produce the quantities of heat mentioned in (4), and (6) the annual saving of coal effected at Hallstra Paper Plant by use of heat-recovery batteries. W. SEGERBLOM

Investigation on the strength of fine paper with special reference to paper of the Swedish government. S. KÖHLER AND G. HALL. *Svensk Pappers-Tid.* 28, 240-3, 269-73, 303-6(1925).—The Government Testing Commission in charge of establishing standards of strength and of manuf. of government paper found it necessary to lay out the following program of tests: (1) under strength: (a) tearing, (b) tensile and (c) folding strength; (2) under chem. const.: (a) Cu no., (b)  $\alpha$ -,  $\beta$ - and  $\gamma$ -cellulose, (c) acidity, (d) ash, (e) resin content, (f) animal glue and casein content, and (g) starch content. Details are given of the different tests used, and tables show the influence of varying conditions of manuf. on the strength of paper. W. SEGERBLOM

Colors used in the paper industry (GINSBERG) 25. Dyeing properties of cotton (TAGLIANI) 25. Ornamenting paper (Brit. pat. 227,202) 25. Impregnating fabrics with wax (Brit. pat. 227,188) 25.

Soluble carbohydrates from cellulose. E. HÄGGLUND. U. S. 1,544,149, June 30. Sawdust or other cellulosic material is treated with a  $\text{HCl}$  soln. of at least about 39% strength, the soln. is sepd. from the residue and the latter is leached with a  $\text{HCl}$  soln. of lower strength.  $\text{HCl}$  gas is dissolved in the resulting leach liquor and the resulting soln. is used for reacting upon a further quantity of cellulosic material.

Dissolving cellulose esters. J. C. CLANCY. U. S. 1,544,809, July 7. Liquid anhyd.  $\text{NH}_3$  is used for dissolving cellulose acetate or nitrate or other cellulose esters. U. S. 1,544,810 specifies liquid  $\text{SO}_2$  for dissolving cellulose acetate or nitrate or other cellulose esters. U. S. 1,544,811 relates to the use of liquid  $\text{SO}_2$  for dissolving cellulose nitrate. U. S. 1,544,812 specifies treating cellulose nitrate with liquid anhyd.  $\text{NH}_3$  to dissolve it and then substantially removing the  $\text{NH}_3$  by evapn.

Cellulose acetate. P. C. SEEL. U. S. 1,544,944, July 7. A moist but self-sustaining pulp of cellulose fibers, e. g., cotton rag stock, is subjected to a picker action to form fiber aggregates which maintain, at least partially, their identity. These aggregates are then dried and treated with acetylating liquid.

Dehydrating cellulose hydrates. J. E. BRANDENBERGER. U. S. 1,544,885, July 7. Air-dried cellulose hydrates are subjected to the action of dry satd. steam.

Reclaiming paper pulp. L. M. BOOTH. U. S. 1,543,663, June 30. The solid particles in "white water" are reclaimed for reuse by adding reagents such as  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{Na}_2\text{CO}_3$ , which will assist in their coagulation and sedimentation; they are then recovered by a special sedimentation and thickening treatment. An app. is described.

Transfer sheet. J. A. L. MÖLLER. U. S. 1,544,675, July 7. A coating of transfer material is applied to one side of a permanently opaque sheet of paper the body of which is so colored throughout as to correspond to the color of the coating, so that the appearance of the sheet is substantially unaltered by the removal of transfer material.

## 24—EXPLOSIVES AND EXPLOSIONS

CHARLES E. MUNROE

The causes of certain phenomena observed in the course of the manufacture of powder. B. M. MARQUEYROL AND P. LORLETTE *Mem. poud.* 21, 276-80 (1924).—Certain grains of powder are of an abnormally dark color and lose a relatively large quantity of their diphenylamine when they are heated. These effects, as well as the inferior stability of the powder, have been traced to impurities present in commercial  $\text{Et}_2\text{O}$ , in particular  $\text{Et}_2\text{O}_2$ ,  $\text{H}_2\text{O}_2$  and  $\text{O}_2$ . A revision of the specifications for  $\text{Et}_2\text{O}$  and a study of the formation of impurities during manuf. and storage are indicated as desirable.

TENNY L. DAVIS

Origin of colored spots in powder B. J. DESMAROUX. *Mem. poud.* 21, 238-58 (1924).—The spots observed on strips of powder stabilized with diphenylamine (I) and the colors which these strips assume in the course of manuf. are due to oxidation of the stabilizer. Oxidation of I in a neutral medium yields tetraphenylhydrazine (II) and "phenazine" (diphenyldihydrophenazine?) (III), in a sulfuric acid medium diphenylbenzidine (IV), and in an alk. medium the mol. is destroyed, while a little diphenylazophenylene is formed. Samples of powder were prepd. from decarbonated nitrocellulose and purified alc. and  $\text{Et}_2\text{O}$ , and contained 1% respectively of (a) I recrystd. from alc., (b) white cryst. II, (c) III, (d) cryst. IV and (e) diphenylnitrosamine (V). The samples were dried in part in a current of air, in part in a current of N, and were then heated at 50° in alc. vapor carried by a stream of N or of air. At 50° in the presence of alc. vapors a blackened in 24 or 48 hrs. in air but remained almost unchanged in nitrogen, a result which shows that the darkening of I in powder is due to the oxidizing action of the air and not due to an oxidation provoked by the nitrocellulose. b, dried in the cold, took on a violet color, and at 50° in alc. vapor darkened rapidly in air, more slowly in N. c commenced to darken during the mixing and was completely black after drying. d showed the same results as a, but more slowly. e remained without apparent change in all the expts., a result which shows that the blackening of the powder is not due to V and from which it is also inferred that the blackening of powder is due to the oxidation of the amino hydrogen of I. It is concluded that the darkening of powder is due to III, and that the darkening of powders contg. II is due to the same cause, for this substance in the presence of solvent at moderate temp. is transformed little by little into III. The black color of powders contg. IV is due to a different substance from that which produces the color in powders containing I and III, for the former gives an emerald-green alc.  $\text{Et}_2\text{O}$  soln. while the latter both give violet solns. The discoloration of powder could be prevented by drying it in an atm. deprived of O.

TENNY L. DAVIS

Improvements in the working of powder B mixtures during the War. ROCHE. *Mem. poud.* 21, 158-70 (1924).

TENNEY L. DAVIS

Humidification of powders at Bergerac. ROCHE. *Mem. poud.* 21, 153-7 (1924).—R describes expedients used during the persistent drought of 1918. T. L. DAVIS

Recovery of solvent in an atmosphere of inert gas. J. DESMAROUX. *Mem. poud.* 21, 227-37 (1924).—Accidents in smokeless-powder solvent-recovery houses may be due to propagation of flame by the gaseous medium or to propagation by the powder itself. Even at 50°, which is higher than the practical temp. of current manuf., the propagation of flame by the solvent vapors (alc. and  $\text{Et}_2\text{O}$ ) in air does not take place if the O content of the air has been reduced to less than 10%. If the O content is less than 8.5%, the mixt. does not propagate its own inflammation. An atm. contg. 5% O would insure perfect safety and would permit the  $\text{Et}_2\text{O}$  concn. to be greatly increased without its becoming explosive.

TENNY L. DAVIS

Determination of solvent in dried powder B. J. DESMAROUX. *Mem. poud.* 21, 211-226 (1924).—A knowledge of the compn. of the "total solvent" in powder after it has been dried in the air, or in the dryhouse, or in the water-drying treatment, is important for following and for comparing these processes. The powder is dissolved by hot aq. KOH distd., and the distillate (special condenser cooled with solid  $\text{CO}_2$ ) analyzed for alc. and  $\text{Et}_2\text{O}$ , by two detns.: (1) lowering of  $\rho$ , which D finds to be proportional to the total number of moles of alc. and  $\text{Et}_2\text{O}$ , and (2) surface tension, measured by the rise in capillary tubes, which D finds to be influenced greatly by  $\text{Et}_2\text{O}$  and much less by alc. Pure nitrocellulose treated by this method gave small figures which were applied as corrections in the regular detns. From ordinary powder diphenylamine distd. over, but was filtered from the distillate without interfering with the detn. The method was checked against known quantities of alc. and  $\text{Et}_2\text{O}$ . Results are reported for

powders air-dried for various periods, water-dried at 60°, and for powder of current manuf.

Studies at the Ripault powder plant of powder driers with hot water circulation. TENNY L. DAVIS  
ANON. *Mem. poud.* 21, 178-207. TENNEY L. DAVIS

The decomposition of trinitrotoluene by the action of sunlight. C. KRAUZ AND O. TUREK. *Z. ges. Schiess-Sprengstoffw.* 20, 49-58(1925).—Com TNT was recrystd. from EtOH to a const. m. p. of 81.4°, dried in a thin layer in the dark and finally over H<sub>2</sub>SO<sub>4</sub>, and the fine white needle crystals were exposed to direct sunlight with occasional stirring, until a uniform brown color was obtained from the action of the light. After 14 days' exposure, extrn with hot H<sub>2</sub>O gave a yellow soln with acid reaction, colored intense red by alkali and giving a dense ppt with nitron acetate. The insol residue was still dark colored. After 4 months' exposure, the m. p. dropped to 73.5°. A C<sub>6</sub>H<sub>5</sub> soln. of the dark TNT was extrd with 5% soln of NaHCO<sub>3</sub> and C<sub>6</sub>H<sub>5</sub>(OH)(NO<sub>2</sub>)<sub>2</sub> (A), and (NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>COOH, (B), were qualitatively identified in the ext. To det. the effect of such impurities in TNT, pure (A) and (B) and their metallic salts of Hg<sup>+</sup>, Hg<sup>++</sup>, Pb, Cu, Ni, Fe, Al, Mn, Zn, Mg, Ba, Ca, K and Na were prepd and mixed with TNT in amts. of 5, 10 and 20%. Impact tests with 2 kg weight, with 0.1 g sample wrapped in tinfoil, showed all of these substances to increase the sensitiveness of TNT. Pure TNT gave complete explosion at 95 cm. With 5, 10 and 20% Pb picrate the results were 70, 50 and 40 cm.; with similar amts. of K trinitrobenzoate 60, 50 and 40 cm. The other salts mentioned increased sensitiveness to a less degree. TNT exposed to sunlight until brown gave an impact test of 75 cm. Its sensitiveness was slightly increased by 5% of metallic Cu or Hg or of their oxides. Data as to quant. detn. of (A) and (B) in TNT will be given in a subsequent paper. C. G. STORM

Methods used by the Germans in loading high-explosive shell. G. C. HALE. *Army Ordnance* 5, 858-40(1925).—To limit exposure to toxic effect, especially with shell fillers such as dinitrobenzene and trinitroanisole, which are especially toxic, the explosives were cast into cardboard cartons, shaped to fit the shell cavity, at the chem works. The cartons were waterproofed by a coating of shellac or by impregnating the cardboard with petroleum pitch. The method of prepn and loading is given in detail.

CHARLES E. MUNROE

The combustion of carbon monoxide mixtures. J. H. CROWE AND A. H. NEWBY. *Phil. Mag.* 49, 1112-31(1925).—Mixts. of CO with air in different proportions were used. A 16 inch sphere with central ignition was provided with a spark-gap arrangement for measuring the velocity by a falling-plate camera. A fan is used to stir the mixt. before firing. Pressures up to 3 atm. were measured by a U-tube and above this by a Bourdon gage. The conclusions are that flame velocity in CO air mixts. is always uniform and in addn. there is a vibratory motion at the flame front. Combustion is not complete when the flame strikes the wall of the explosion vessel. Instantaneous heat addn. at any point can be approached but never attained. Convection currents do not play an important part even in the weaker mixts. The max. of velocity, pressure and temp. occurs with a rich mixt. contg. about 40% CO. The phenomena can be explained by dissociation. The cooling loss is a min. with 45% CO and increases greatly as the upper and lower limits are approached. Increase of initial pressure greatly decreases the inflammability of CO and air. Inert gas causes a lower flame velocity and slower subsequent combustion. S. C. LIND

New method of flame analysis. O. C. DEC. ELLIS AND H. ROBINSON. *J. Chem. Soc.* 127, 760-4(1925).—The revolving-film method of photography does not show the shape of the flame front at any stage of its propagation and the modification of the method by Mason and Wheeler does not help much if the speed of the flame is irregular. The app. described here can be used to secure a snap shot of the flame at any interval of time. If the flame is moving along a tube, a no. of snap shots, showing consecutive phases of the propagation, can be taken on one plate. The most important element is a revolving shutter, consisting of a steel disk, 0.64 meter in diameter, from the periphery of which 24 small windows have been cut at regular intervals. This disk can be rotated at any desired speed and one or more windows used for taking a picture or pictures. W. T. H.

Liquid-oxygen blasting cartridges. G. C. LEWIS. U. S. 1,544,247, June 30. A body of lampblack or similar finely subdivided combustible material is satd. with liquid O<sub>2</sub> and placed in a loose-fitting cover of paraffined paper or other material substantially impermeable to liquid O<sub>2</sub>.

Explosive cartridge. A. C. SCOTT. U. S. 1,543,798, June 30. A cartridge of the

Sprengel type comprises 2 concentric tubes between which crystals such as  $\text{KClO}_3$  are packed so that the vol. of the voids between the crystals does not exceed 32% of the vol. occupied by the crystals. In use the voids are filled with a light hydrocarbon oil. Cf. C. A. 18, 2964.

Explosive cartridge. G. B. HOLDERER. U. S. 1,543,850, June 30. A cartridge for use with liquid O comprises an inner wrapper of paper and an outer wrapper of textile material impregnated with linseed oil or other  $\text{H}_2\text{O}$ -repellent substance, with a filling of carbonaceous material. U. S. 1,543,851 specifies a cartridge with an inner wrapper of textile material, and an outer wrapper of frangible material such as paper. When the outer wrapper is broken, the inner wrapper expands and holds the filling of carbonaceous material.

Charging rockets. R. M. BUTT and A. BROCK. Brit. 227,355, June 4, 1924. The propelling compn. of rockets, to facilitate charging, is mixed with  $\text{H}_2\text{O}$ , starch or flour paste, oil or graphite.

## 25--DYES AND TEXTILE CHEMISTRY

L. A. OLNEY

Azo dyestuff technology. I. The manufacture of Orange II. CLEMENT WHITE-HEAD. *Chem. Trade J.* 77, 33-4 (1925). E. H.

New American, Continental and British dyestuffs of 1924. JAMES FERGUSON. *Textile Recorder* 43, No. 507, 67-9 (1925).—A brief description of 110 new dyes. CHAS. E. MULLIN

Cotton dyes fast against perspiration. W. SANDERSON. *Textile Colorist* 47, 430 (1925).—A list of dyes is given. CHAS. E. MULLIN

Dyes fast against bleaching. W. R. MCKENNON. *Textile Colorist* 47, 383 (1925).—A list of dyes is given. CHAS. E. MULLIN

After-treatments with azophor red and azophor orange MN. W. J. CHESTER. *Textile Colorist* 47, 374 (1925).—The dyes and formulas are given. C. E. MULLIN

Analysis of dye mixtures by means of titanous chloride. W. C. HOLMES. *Am. Dyestuff Rept.* 14, 415-8 (1925).—Titrations of various dyes with  $\text{N TiCl}_3$  are tabulated for 42 tests. From the analytical results a general formula was deduced which may be applied in testing mixts. of dyes. L. W. RIGGS

New developments in Naphthol AS. E. J. RATH. *Proc. Am. Assoc. Textile Chem. Colorists* 1925, 146-8. *Am. Dyestuff Rept.* 14, 426-8. —A lecture followed by discussion. L. W. RIGGS

Standard dye samples. C. F. GREEN. *Textile Colorist* 47, 381 (1925).—A composite sample from each delivery is recommended for the standard. C. E. MULLIN

Making up colors for printing. W. SANDERSON. *Textile Colorist* 47, 382-3 (1925).—General. CHAS. E. MULLIN

Colors used in the paper industry. ISMAR GINSBERG. *Textile Colorist* 47, 383-5 (1925).—The various dyes and their uses in paper are discussed. CHAS. E. MULLIN

Shoe-dye poisoning. C. W. MUEHLBERGER. *J. Am. Med. Assoc.* 84, 1987-8 (1925).—Nine new cases are reported, 6 of which were caused by aniline instead of the more usual nitrobenzene. State or national regulations should prohibit the use of these poisons in shoe dyes. L. W. RIGGS

Logwood black on various materials. H. R. TISDALE. *Textile World* 67, 3545-7, 3551-3 (1925).—A general discussion of the methods and formulas for the application of logwood to silk, wool, cotton, rayon, leather, wood and bone. CHAS. E. MULLIN

Practical hints on the production of bright colors on textile fabrics. RAFFAELLE SANSONE. *Am. Dyestuff Rept.* 13, 101-6, 218, 233-6, 276-8, 328-30, 336-9, 498-9, 505-6, 524-8, 564-5, 571, 653-6, 797-9 (1924), 14, 93-5, 124-6, 234-7, 271-3, 374-6, 440-2, 469-71 (1925).—Dyes, plants, machinery and methods of procedure are treated with much detail in this paper the first installment of which appeared Feb. 11, 1924. The work is still in progress. L. W. RIGGS

Dyeing acetate silk. C. E. MULLIN. *Am. Dyestuff Rept.* 14, 173-6, 214-5, 237-8, 243-5, 278-81, 315-8, 345, 350-2, 379-81, 410, 420-4, 469-8 (1925). L. W. R.

Dyeing of cotton piece goods with acid coloring matters. J. M. MATTHEWS. *Color Trade J.* 16, 123-6 (1925); cf. C. A. 19, 2415.—Variations of the Al soap mordant on cotton for acid dyes may be obtained by giving the fabric a tannic acid bath before soaping, or by adding gelatin to the soap bath. Zn or Sn may be used in place of the Al. Sol. blues are used for blueing bleached cotton, and eosin dyes for pink tinting. The eosin colors may be brightened with Turkey red oil. CHAS. E. MULLIN

**New dyeing properties of cotton.** G. TAGLIANI. *Textile World* 67, 3547-9(1925).—A discussion of the properties, particularly as to dyeing, of the various cellulose esters. Cellulose treated with *p*-toluenesulfonyl chlorides, marketed as *immunized cotton*, resists the direct dyes, but is dyed by the basic, certain acid, and gallocyanine dyes. It absorbs diazotizable amino bases from soln. and in some respects resembles acetate silk in its dyeing properties. It can therefore be used for colored-effect threads in cotton, wool and union materials. The immunizing process may be carried out locally, or a cellulose *p*-toluenesulfonic ester may be printed on the material. C. E. M.

**Study of cotton neps.** GEO. BUTTERWORTH. *Textile World* 67, 3867(1925).—Microscopic examn. of cotton neps shows them to be composed of under-developed fibers, generally equal in length to the av. but unusually flat and translucent, and in many instances still attached to portions of the rudimentary coats of aborted seed. Five illus. CHAS. E. MULLIN

**Improving alkali test for cotton-wool mixtures.** ANNA F. HEDRICK. *Textile World* 67, 3725-9(1925).—If peeler cotton is boiled under a reflux condenser with a 5% NaOH soln. it loses 5.34% in 0.5 hr., 5.61% in 1 hr. and 5.5% in 2 hrs. The loss increases rapidly with temp. but, less with increased NaOH concn. (up to 10%); H<sub>2</sub>O alone gives a 1.5% loss in 0.5 hr. or 2% in 2 hrs. When the cotton is pretreated with 1% HCl it loses over 2% in 5 min., over 3% in 0.5 hr. and about 4.25% in 1 hr. When the acid-treated cotton is heated with 5% NaOH at 90-95°, the loss of cotton is much greater than that with untreated cotton, amounting to almost 5% in 0.5 hr. and 8.5% in 1 hr.; or a total loss by acid and alkali treatments of 6% in 5 min., about 11.2% in 0.5 hr. and about 16.2% in 1 hr. Samples receiving a long acid treatment varied so much in results, that it is recommended to limit the acid treatment to not over 10 min. Various grades of cotton give different losses with 5% NaOH soln., lower grades losing as much as 2% more than the better grade. The method recommended is to condition a 2-g. sample for 2 hrs. or more at 21° and 65% relative humidity, and weigh. Boil moderately in about 100 times its wt. of 5% NaOH for 1 hr. in a 400-cc. assay flask with a reflux condenser. Filter through wire cloth, wash with H<sub>2</sub>O, then with 3% AcOH, and finally with hot H<sub>2</sub>O. Dry at 45-50° for 20 min., let stand overnight in the open air and condition at 21° and 65% humidity as before. Results check to ± 0.3% on duplicate samples, and should be corrected by 5.6% for loss of cotton. Four charts and two tables are given. CHAS. E. MULLIN

**Moisture relations of cotton.** The absorption of water by cotton mercerized without tension. A. R. URQUHART AND A. M. WILLIAMS. *J. Textile Inst.* 16, 155-66T (1925); cf. C. A. 19, 893, 1631.—The variations in water-fixing power of mercerized cotton with the concn. of the mercerizing soln. employed are strikingly similar to the variations in dimensions of the unit hairs. Thus when mercerized with 15% NaOH or 28% KOH, which solns. are known to produce the max. swelling, the cotton also has a max. hygroscopicity. On the other hand, the ratio between the moisture content the mercerized and unmercerized scoured cottons at the same atmospheric humidity is independent of the degree of that humidity. When mercerized with 15% NaOH the regain is about 1.57 times as great when the material is absorbing moisture, and 1.46 times as great when losing moisture, as the regains of unmercerized cotton no matter what the prevailing humidity may be. Mercerization increases the accessible surface of the cotton in proportion to the mercerization ratio, which, therefore, might be used as a measure of the absorptive capacity of the material for dyes as well as water. L. W. RIGGS

**Soluble antimony compounds.** C. F. GREEN. *Textile Colorist* 47, 379-80(1925).—Practical tests are described to det. the ability of Sb compds. to fix tannic acid on cotton as a mordant for basic dyes. CHAS. E. MULLIN

**Bleaching textiles with chlorine and its compounds.** J. C. BAKER. *Proc. Am. Assoc. Textile Chem. Colorists* 1925, 151-3; *Am. Dyestuff Rept.* 14, 451-3.—The paper deals mainly with bleaching by means of NaClO. L. W. RIGGS

**A note on iron stains.** C. F. GREEN. *Textile Colorist* 47, 381(1925).—The Fe stain on a fabric is "activated" with concd. HCl before making the usual K<sub>4</sub>Fe(CN)<sub>6</sub> test. CHAS. E. MULLIN

**Backwashing worsted sliver.** TOLLER. *Textile World* 67, 3422-3(1925).—General. CHAS. E. MULLIN

**Rejto method of testing cloths.** JOSEPH BERCSL. *Textile World* 67, 2992-3(1925); cf. C. A. 19, 2417.—A description of the Rejto cloth testing machine, the diagrams of cloth performance obtain with it and the applications of these diagrams. C. E. M.

**Method of testing knitted fabric.** F. R. MCGOWAN AND C. H. HAMLIN. *Textile*

World 67, 3285-7(1925)—A description of the method proposed by the Bureau of Standards which consists of a 1" X 1" grab on a 4" X 5" specimen with a speed of 12" per min  
CHAS E. MULLIN

Importance of good scouring in the bleaching of cotton and linen fabrics. WM. KIRK *Textile Colorist* 47, 359-62(1925)—General.  
CHAS E. MULLIN

Solvents for use in the cleaning of dyed garments. J. MERRITT MATTHEWS. *Color Trade J* 15, 173-6(1924), 16, 17-20(1925)—The use of gasoline, CCl<sub>4</sub>, benzene, C<sub>6</sub>H<sub>6</sub>, tetralin and turpentine as dry-cleaning solvents is discussed, as well as benzene soaps  
CHAS E. MULLIN

A semi-non-inflammable dry-cleaning solvent. J. W. "DIXIE" STODDARD. *Canadian Colorist and Textile Processor* 5, 180-2(1925)—A naphtha boiling between 138° and 215.5° is recommended  
CHAS E. MULLIN

Dyes. J. BADDILEY W. W. TATUM and BRITISH DYE STUFFS CORPORATION, LTD. Brit. 227,923, Oct. 25, 1923 Acid dyes giving blue to green shades on wool or "acetyl silk" are obtained by condensing 4,8-dihalogenanthraquinone with 2 mol proportions of an aminobenzoic acid, or by condensing 4,8-dinitro-1,5-dichloroanthraquinone with 2 mol. proportions of an aminobenzoic acid and reducing the NO<sub>2</sub> groups. Examples are given.

Dyes. J. FRÖLICH U. S. 1,544,441, June 30 Dyes which produce various colors on wool are prep'd by reaction of thionyl chloride upon 2,5-diarylbenzoquinones

Vat dyes. A. LÜTTINGHAUS and F. KACER U. S. 1,544,095, June 30. Vat dyes dyeing cotton greenish yellow are formed from a 1-mercapto-2-aminoanthraquinone and glyoxal or a glyoxal comp'd

Vat dye. P. NAWIASKY and W. KRANNICH. U. S. 1,544,924, July 7. N-Dihydro-1,2,1',2'-anthraquinoneazine is first chlorinated in a dry state and the chloro deriv. thus obtained is brominated in conc'd. H<sub>2</sub>SO<sub>4</sub> soln to produce a vat dye which is fast both to Cl and to calcareous waters

Monoazo dyes. A. L. LASKA and A. ZIRSCHER. U. S. 1,545,335, July 7. The diazo comp'd of 5-nitro-*o*-toluidine is combined with a *p*-alkoxyarylide of 2,3-hydroxynaphthoic acid to produce red powders insol in H<sub>2</sub>O which yield lakes fast to light. When produced on the fiber the dyes give fast bluish red shades.

Trisazo dyes. FABRIQUE DE PRODUITS CHIMIQUES, CI-DEVANT SANDOZ. Brit. 227,440, Jan. 11, 1924 Trisazo dyes are formed by coupling a diazo comp'd of the benzene or naphthalene series with a second component, rediazotizing and coupling again with a second component, then further diazotizing and coupling with a 1-arylaminonaphthalenesulfonic acid. The dyes thus obtained dye cotton directly gray, blue gray or black shades fast to light and washing. Numerous examples are given.

Dyeing. M. SCHOLTZ U. S. 1,544,603, July 7. The colors are fixed in dyed materials by quickly passing them through a hot aq. saline soln. contg. a small proportion of HOAc.

Dyeing. AKT.-GES. FÜR ANILIN-FABRIKATION. Brit. 228,112, Jan. 23, 1924. Furs, skins, hair, feathers, etc., are dyed fast olive-brown by treatment with 4-chloro-1,2-diaminobenzene in the presence of an oxidizing agent such as H<sub>2</sub>O<sub>2</sub>. Skins may be preliminarily mordanted in a bath contg. HOAc and CuSO<sub>4</sub> or FeSO<sub>4</sub> or CuSO<sub>4</sub> and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>.

Dyeing. A. ESCHACH and J. P. WORMS. Brit. 227,907, Oct. 22, 1923. Pinks and reds are produced on silk by reduction of Fehling soln. with glucose and other dyeings are similarly effected by use of metallic comp'ds. and reduction with aldehydes, ketones, sugars, hydroxylamine, hydrazines or their salts, the metallic comp'd. used being originally retained in an alk. medium by added substances.

Dyeing with ferricyanides, ferrocyanides, etc. A. ESCHACH and J. P. WORMS. Brit. 227,906, Oct. 22, 1923. Fibers, leather, hair, etc., are colored by reduction, in a slightly acid medium, of ferricyanides or ferrocyanides in the presence of traces of acid Hg sulfate such as Denigès reagent. Wool, silk or cotton is colored blue with sugar, acid Hg sulfate and K<sub>3</sub>Fe(CN)<sub>6</sub>. Ferrocyanides produce lighter colors. Sugar, glucose, CH<sub>2</sub>O, formic acid, catechol, resorcinol, hydroquinol, naphthols, aniline salts, dextrin, sol. starch, tannins and saponins may be used as reducing agents.

Dyeing artificial silk. R. LAVALD. Brit. 227,834, Jan. 16, 1924. Artificial silk is dyed with black polyazo and other substantive dyes in a bath contg. Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>SO<sub>3</sub>. The goods are immersed at a temp. of 50°, heated to 70°, withdrawn, cooled to 40°, HOAc is added and the goods are then reimmersed and the temp. is raised to 65° to produce a glossing effect.

Apparatus for dyeing, etc., yarn in wound form. J. T., and J. BRANDWOOD. Brit. 227,201, Oct. 12, 1923.

Apparatus for mercerizing yarn in hanks. NIEDERLAHNSTEINER MASCHINEN-FABRIK GES. Brit. 227,841, Jan. 14, 1924.

Dyeing cellulose acetate. L. A. LEVY Brit. 227,146, Oct. 19, 1923. A soln. of cellulose acetate in acetone is treated with a dye and then subjected to dry spinning.

Dyeing cellulose acetate. BRITISH CELENESE, LTD. and G. H. ELLIS. Brit. 227,183, Oct. 9, 1923. Cellulose acetate yarns, threads, fabrics or films are dyed, printed or stenciled by use of unreduced vat dyes of the anthraquinone series which have been solubilized by pretreatment with sulfotrimaleic acid or other solubilizing agents as described in Brit. 219,349 (C A 19, 579). Algal pink R may be used and different dyes may be used together for mixed goods. Cf C A 19, 1351.

Cellulose acetates for artificial silk, etc. J. O. ZOANOWICH Brit. 227,134, July 4, 1923. Directly spinnable cellulose acetate acetylation solns or mixts are rendered stable as to viscosity by adding  $H_2O$  or other stabilizer such as aq. MeOH, EtOH, AmOH, lactic or formic acid, chloral hydrate,  $H_2O_2$  or glycerol. Solns thus prepd. remain in spinnable condition for several weeks.

Artificial threads. J. E. BRANDENBERGER U. S. 1,544,631, July 7. Lustrous hollow threads or filaments are formed from a soln. of "mildly-ripened" viscose.

Artificial threads, etc., from viscose. A. KAMPE U. S. 1,545,144, July 7. In forming threads, films, ribbons or the like, viscose is extruded into an aq. soln. of a sulfonic acid of a condensation product obtained by sulfonating the condensation product of phenol with formaldehyde.

Reclaiming cotton from oily wastes, etc. AMERICAN LAUNDRY MACHINERY CO. Brit. 227,253, Nov. 27, 1923. The oil is extd. from journal box waste or similar oily waste and it is then tumbled in a current of air to remove sand, dirt, metal particles and short fibers and prep. it for reuse.

Impregnating fabrics with wax. J. W. BARDSLEY. Brit. 227,188, Oct. 10, 1923. Aq. colloidal emulsions of waxes, tallow or shellac are used for treating textile fabrics, felt for hats, calico in calico printing, paper pulp, leather, candle wicks, etc.

Coating textile fabrics. H. L. ROTHBAND and J. MANDLEBERG & Co., LTD. Brit. 227,527, Oct. 17, 1923. Artificial silk is treated with paraffin, stearin, Japan wax or spermaceti, before or after coating with rubber, and may also be treated with Al formate or acetate or similar salt.

Finishing cotton or similar fabrics. J. HUEBNER Brit. 227,480, July 18, 1923. A fabric is treated with an ammoniacal Cu oxide cellulose soln. and is then mercerized with or without tension and before or after treatment to remove the Cu. Pigments, mordants, resists, etc., may be used in connection with the process and treatment with  $H_2SO_4$  or HCl of greater strength than used in ordinary souring may be employed instead of mercerization. Transparent or crepe effects may be obtained by special treatments which are described.

Finishing textile fabrics. J. HUEBNER. Brit. 227,370, July 12, 1923. Cotton, linen, wool or silk fabrics are printed or padded with a soln. of cellulose in ammoniacal Cu oxide and are treated with a pptg. agent which produces differently colored ppts. from the Cu compd.  $NH_4$  molybdate gives light green,  $NH_4$  vanadate a yellowish green, Rongalite a yellowish brown and NaOH or soap solns. a dark brown. Other examples are given. Fabrics which have been mercerized may be given this treatment.

Ornamenting fabrics, etc. N. M. TEMPLE and F. C. O. SAY. Brit. 227,202, Oct. 12, 1923. A design pattern in body color of a pasty consistency is formed on textile fabric, wood, paper, etc., tinted by oils and then treated with finely divided glass.

Bleaching, etc., slivers. SOC. A. DECSAMPS Brit. 227,459, Jan. 10, 1924. Fibers are subjected to lye treatment, cream coloring or bleaching in the form of slivers or rovings and before they pass to the roving and spinning frames. An app. is described.

Retting flax. SOC. POUR L'APPLICATION INDUSTRIELLE DES BREVETS PEUFAILLIT. Brit. 227,836, Jan. 16, 1924. Flax or similar material is boiled in a bath of  $H_2O$  contg. a small quantity of gasoline mixed with a portion of liquor from a previous retting operation.

Fire-proofing artificial silk. R. LAVAUD. Brit. 227,855, Jan. 16, 1924. The material is impregnated with a soln. of  $NH_4$  carbonate and sulfate,  $H_3BO_3$ , borax and starch.

## 26—PAINTS, VARNISHES AND RESINS

A. H. SABIN

Latent heat of vaporization of lacquer solvents. H. A. GARDNER AND H. C. PARKS. Paint Manufs. Assoc. of U. S., *Circ.* No. 236, 275-81(1925).—To afford information on the relative tendency of lacquer solvents to reduce the temp. of the film below the dew point, and thereby cause "blushing," a dish filled with the solvent was placed in front of an electric fan, and the drop in temp. noted every 30 sec. The losses in temp. for various single and mixed solvents are tabulated and plotted.

F. A. WERTZ

Vapor pressure of lacquer solvents. H. C. PARKS AND H. A. GARDNER. Paint Manufs. Assoc. of U. S., *Circ.* No. 237, 282-8(1925).—Review with vapor-pressure graphs.

F. A. WERTZ

Electrolytic production of Fe oxide pigments (Brit. pat. 227,319) 4.

Paint for use on metals. E. F. MORRIS AND J. A. MORRICE. Brit. 227,026, Oct. 26, 1923. Rusting of Fe or other metals is inhibited by first coating them with an aq. compn. which may contain basic Zn chromate, glue, gum and H<sub>2</sub>O (with or without turpentine or "white spirit") and then applying a paint preferably also contg. basic Zn chromate in linseed oil or a similar vehicle.

Composition for polishing varnished surfaces. J. H. NUNAN. U. S. 1,545,272, July 7. "Butter of antimony" 4 oz., raw linseed oil 1 qt., Chinese wood oil 1 qt., oil of citronella 4 oz., cedar oil 4 oz., turpentine 1 pint, HCl 7 oz., oxalic acid 7 oz. and alc. 1 qt.

Synthetic resins. CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE GES. Brit. 228,157, Jan. 23, 1924. Condensation and polymerization products of C<sub>2</sub>H<sub>2</sub> are produced by reacting with C<sub>2</sub>H<sub>2</sub> upon substances such as CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, xylene, C<sub>6</sub>H<sub>6</sub>, hexalin, alcs, glycols, phenols, chlorides, carboxylic acids and their esters. Salts of Hg or Al may be used as catalysts and acids or alkalis may serve as activators. Under different conditions products may be obtained which are either of the cuprene or the aldehyde resin type. Numerous examples are given. Cf. C. A. 18, 594.

Compositions containing synthetic resins. CANADIAN ELECTRO PRODUCTS CO., LTD. Brit. 227,216, Oct. 18, 1923. Fibrous or cellular material is incorporated with a phenol acetylene condensation product and the mass is converted into a dense hard body by subsequent treatment. The condensation product described in Brit. 183,830 may be used and may be given a preliminary treatment with an aldehyde. (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub>, a phenylenediamine or surfuramide may be used as hardening agents, heat and pressure being employed.

Phenol-aldehyde condensation products. J. KOSTAL, J. NOVAK AND REGAL & CO. Brit. 227,468, Jan. 12, 1924. O<sub>3</sub> or ozonides (e. g., sandarac ozonide or ozonized pinene) are used as catalysts in making artificial phenol-aldehyde resins.

## 27—FATS, FATTY OILS, WAXES AND SOAPS

E. SCHERUBEL

The seeds of *Citrullus vulgaris* as a source of oil. ANON. *Bull. Imp. Inst.* 23, 149-57(1925).—Analysis of water-melon (*Citrullus vulgaris*, Schrad.) seed from Northern Territories, Gold Coast (locally known as "Neele" or "Niri" seed). Western Province, Gold Coast, Appolonia, Gold Coast (locally known as "Kogai" or "Egusi"), and Nigeria (locally known as "Guna") gave the following results: H<sub>2</sub>O 6.4-8.3, yield of oil (extn. with light petroleum) 33.8-45.3, yield of oil on dry basis 36.8-48.4%. Analysis of the oils gave: d<sub>4</sub><sup>20</sup> 0.9218-0.9236, n<sub>D</sub><sup>20</sup> 1.4645-1.467, acid no. 1.3-17.8, sapon. no. 191.3-195.1, I no. (Hübl, 17 hrs.) 113.1-124.3, titer test 29.2-33.4°. "Guna" oil prep'd locally by the natives had d<sub>4</sub><sup>20</sup> 0.9234, n<sub>D</sub><sup>20</sup> 1.465, acid no. 3.8, sapon. no. 190.1, I no. (Hübl, 17 hrs.) 115.5, unsaponifiable 0.9, titer test 35.3°. Analysis of the residual meals (calcd. to 7% fat content) gave: H<sub>2</sub>O 8.6-10.1, crude proteins 23.2-58.8, fat 7.0, N-free ext. 8.3-14.3, crude fiber 12.2-39.2, ash 3.9-4.9, nutrient ratio 1.041 to 1:0.97, food units 99-167. All meals were free from cyanogenetic glucosides. An unidentified alkaloid was found in the meal of one of the samples from Northern Territories, Gold Coast. The oils

are of the semi-drying type, could be readily refined for edible purposes, and could be used as a substitute for cottonseed oil for nearly every purpose. A. P.-C.

Bellier's modified test for peanut oil. H. D. RICHMOND AND A. D. POWELL. *Analyst* 50, 285(1925).—It is probably unsafe to rely on B.'s test without sepp. the fatty acids and taking the m. p. after repeated crystn. W. T. H.

Bellier's modified test for peanut oil. H. A. CAULKIN. *Analyst* 50, 285(1925).—It is not safe to infer the presence of peanut oil in olive oil merely on the evidence of B.'s test. In doubtful cases confirmation should be obtained by the Renard test or one of its modifications. W. T. H.

Distinctive characteristics of safflower and sunflower seeds and press cakes. VIZERN AND GUILLOT. *Ann. fals.* 18, 284-6(1925).—So-called "white sunflower" (safflower, *Carthamus tinctorius*) seed from India and Egypt, and "gray Carthamus" from Bombay have practically the same chem. compn. as those of true sunflower (*Helianthus annuus*) seed, as have also the oils obtained from them. The morphological differences of the seeds are briefly outlined. The press cakes can be differentiated by microscopic examn. of the pericarp tissues, which are discussed. A. PAPINEAU-COUTURE

Clarification of wool scourers' effluent and recovery of wool fats. JEAN DE RAEVE, *Ind. Eng. Chem.* 17, 837-8(1925).—The effluent is agitated with steam in a vat and 1 lb. of  $\text{Ca}(\text{OH})_2$  in 1 gal.  $\text{H}_2\text{O}$  is added for every 100 gal. effluent and then filtered, after which  $\text{Cl}_2$  is added as detd. by titration of alkali in the waters. The chlorinated waters are titrated with  $\text{H}_2\text{SO}_4$  to det. the amt. needed to change the hypochlorites into hypochlorous acid. After this is added all the fats rise to the surface and are skimmed. The white foam contg. grease which forms during chlormation is added to the fats and the two heated and filtered. E. SCHERUBEL

The melting point determination of cacao butter. HEINRICH FINCKE. *Z. angew. chem.* 38, 572(1925).—The variations in m. p. of fats are partly due to varying time and conditions of crystn. It is recommended that the fat be cooled slowly and with stirring. The av. of 4 detns. by use of a capillary tube of different samples of cacao butter after 0.66, 2.5, and 14 days, resp., was  $32.3^\circ$ ,  $32.3^\circ$  and  $32.6^\circ$ . C. G. KING

Idrapidsalter. M. GELBER. *Z. deut. Öl-Fett-Ind.* 45, 317-8(1925).—Analytical results of the Idrapidsalter are as follows: Aromatic sulfonic acid 88.7%,  $\text{H}_2\text{O}$  7.7, free  $\text{H}_2\text{SO}_4$  5.66%. Comparative expts. for its hydrolytic power on the basis of equal sulfonic acid and free  $\text{H}_2\text{SO}_4$  show that the "Kontaktsalter" acts 100-150% more rapidly. P. ESCHER

Standard technical specifications for soaps. ANON. *Z. deut. Öl-Fett-Ind.* 45, 318-23, 330-4(1925).—The German Government Committee of Economic Production A. W. F. (Anschluss für wirtschaftliche Fertigung) offers for criticism specifications for soaps and soap powders, edited by J. Davidsohn. P. ESCHER

Theory and practice of the manufacture of soap base. C. BERGELL AND L. LASCARAY. *Seifensieder-Ztg.* 52, 451-2, 471-2(1925).—This article is an attempt to incorporate into the practice of soap making recent progress in its theory, giving popular explanations of the latter and directions for each day's work at the soap kettle, finishing a change in 5 days. P. ESCHER

New ways for the preparation of solid solvent-soaps. H. KASARNOWSKI. *Seifensieder-Ztg.* 52, 452-3(1925).—K. recommends the use of "Diaphanoel" a combination of methylhexalin with the fatty acid from a vegetable oil which has lost almost completely the characteristic odor of methylhexalin and causes semi-transparency when small quantities are used and complete transparency with large quantities, and also imparts to soaps the property of absorbing such solvents as benzene, benzene, turpentine, etc. P. ESCHER

Sapin, a new superfatting agent. G. KNIGGE. *Z. deut. Öl-Fett-Ind.* 45, 306-8, 329-30(1925).—To prevent alky. and to produce smoothness in medicinal and toilet soaps, an addition of lanolin or beeswax is usually made. Analysis of the new agent "Sapin" shows it to be a mixt. of Japan wax with a heavy mineral oil (vaseline or paraffin oil). The method of analysis is given in detail. P. ESCHER

Soap bleaching with persulfate with special reference to an after-treatment with reducing agents. H. NASR. *Seifensieder-Ztg.* 52, 493-4(1925).—Dark hardened fatty acids and dark vegetable oils are bleached by 1%  $\text{K}_2\text{S}_2\text{O}_8$ , but an after-treatment with 0.5% "Blankit" causes a complete reversion in color, even when the soap is salted out after oxidation. Dark brown bone grease, tallow and dark grease from rendering works lose their bleach effect only in part when treated with Blankit, but when the bleached soap is first salted out and then reduced the bleach effect is increased and a nearly white soap results. Dark fatty acid from coconut or palm-kernel oil had a slight yellow under-

tone after the persulfate oxidation, thus disappeared by direct treatment with Blankit and produced a pure white. N recognizes 3 groups of raw materials for soap making with reference to their behavior (1) Oxidation causes insol impurities to become sol; this soly is reversed on reduction (2) Colored impurities become colorless by oxidation, but revert in color on reduction (3) Colored compds are changed to neutral tints and remain neutral on reduction P. ESCHER

Evaluation of bleaching earths. H MIELCK. *Seifensieder-Ztg* 52, 495-6(1925) — For a fuller understanding of the bleaching process by absorption M. suggests the following research work: systematic analyses of the earths, comparison of the ratio of basic oxides to  $\text{SiO}_2$  hydrate, detn of the bitumen content; a study of absorption skins and exchange reactions, removal of Mg soaps, etc., by  $\text{SiO}_2$  hydrate to prevent disturbances during N hardening, a geological study of the deposits; the use of Normann's fat-hardening beaker and the use of inert gases for bleaching expts. P. ESCHER

Reclaiming cotton from oily wastes (Brit. pat. 227,253) 25. Purifying oils (Brit. pat. 227,177) 22.

DUBOVITZ, HUGO. *Chemische Betriebskontrolle in der Fettindustrie*. Berlin: J. Springer. 136 pp bound. G. M. 6. Reviewed in *Ind. Eng. Chem* 17, 877(1925).

LEATHES, J. B. and RAFFER, H S: *The Fats*. 2nd ed. enlarged. London: Longmans, Green & Co. 242 pp. 12s. 6d net. Reviewed in *J. Roy. Soc. Arts* 73, 797; *Chem. News* 130, 413(1925).

Cod-liver oil. D. A. HANSEN. Brit. 227,474, Jan 11, 1924. Cod liver and other fish oils and similar oils are obtained in 1-10 hrs by rendering the pulped and washed cod livers or other raw material at 30-50°, preferably with exclusion of air. The oil may be maintained for some time at 40-50° and inert gas passed through it to remove volatile impurities.

Soap containing potato pulp. R. M. PERRY. U. S. 1,544,103, June 30. Potato pulp is heated with caustic alkali at about 99° for 10-20 min.  $\text{Na}_2\text{CO}_3$  and coconut oil or other saponifiable oil are then added and the materials are mixed at about the same temp for 10-20 min. U. S. 1,544,104 specifies the use of a fatty acid instead of a saponifiable oil, in an otherwise similar process.

Detergent. J. F. MOSELEY. U. S. 1,544,588, July 7. A semi-liquid emulsion is formed of soap, bentonite and tetrahydronaphthalene, tetrahydro- $\beta$ -naphthol, or similar hydrogenated aromatic compd. of high b. p.

## 28—SUGAR, STARCH AND GUMS

F. W. ZERBAN

Progress of the raw-sugar industry. W. V. H. DUKE. *Facts About Sugar* 20, 664-5(1925) — A review of some of the notable factors contributing to the increase of efficiency in the Hawaiian sugar factories T. MARKOVITS

Deterioration of raw sugars in storage. WM L. OWEN. *Facts About Sugar* 20, 442-4(1925); cf. *C. A.* 19, 1789 — O describes the microflora such as mold fungi, yeasts and bacteria occurring in the sugar and their roles in connection with changes in compn. *Ibid* 518-20 — O remarks on the significance of the no. of microorganisms present in sugar with reference to the keeping quality of the same. *Ibid* 566-8 — There are typical changes in the compn of raw sugars induced by the action of various organisms T. MARKOVITS

Report on meeting of Technical Advisers in the Java Sugar Industry, Nov. 18, 1924. ANON. *Arch. Suikerind.* 33, Part 4(1925); cf. *C. A.* 19, 413. Joint meeting of all sections, 3-6; Joint meeting of Chemical and Technical sections, 6-15; Meeting of Chemical section, 18-9. Meeting of Technical section, 19-24. — A round table discussion on the same subjects as at the previous meeting, with following agenda added: use of run-offs for washing sugar; molasses desugarization by means of baryta; caking of sugar; prepn of milk of lime F. W. ZERBAN

Experiment station work and methods in Java. S. N. QUAR. *Facts About Sugar* 20, 614-5(1925) — Opening of the new buildings of the centralized station at Paseroean and a history of 40 yrs' activity of the expt. station T. MARKOVITS

Cane handling and transport in Java. S N QUAR. *Facts About Sugar* 20, 474 (1925).—The paper points out that introduction of mech devices has proceeded slowly because of abundance of cheap labor  
T. MARKOVITS

The sugar exhibition at Magdeburg. G MIKUSCH *Facts About Sugar* 20, 556 (1925).—Comprehensive display of methods and equipment used in beet-sugar production.  
T. MARKOVITS

The development of the German beet-sugar industry. P. BECKER *Chem. App.* 12, 84-5, 115-6(1925)  
J. H. MOORE

Use of indicators in sugar-house control. H A COOK *Facts About Sugar* 20, 592-4(1925).—Methods and substances are described that are employed to give high degree of accuracy in color tests of juices. C suggests that the colorimetric spot test method should be used in detg the acidity in the raw and clarified juices. Methods of detn. and the indicators and their use are discussed and the equipment required is given. C. concludes that the adoption of the suggested method will not be a cure-all for the trouble in the cane-sugar practice. It will, however, be a step far in advance of the present practice and will eliminate much of the guess work in factory control.  
T. MARKOVITS

Deterioration of cane mill juice from the aspect of acidity increase. W. L. McCLEERY. *Facts About Sugar* 20, 520-1(1925).—A report is given on sucrose losses due to bacterial action and the effects of increased care in cleaning mills. During the 1923 crop it was noticed that juice expressed by the lab. mill was much lower in acidity than that of the mixed juice, pointing to the fact that the acidity must be increasing in the milling plant. By analyzing composite samples from each mill, macerators, tanks, supply pipes, etc., it was evident that the increase in acidity and the subsequent losses due to this action were much larger than had been the prevailing opinion.  
T. M.

Fine straining of raw juice. D. G. CONKLIN *Facts About Sugar* 20, 470-2 (1925); cf. C. A. 19, 1939.—The theory of fine straining and the effects on boiler-house work are reported.  
T. MARKOVITS

Studies on liming and carbonating beet juices. G. CAPELLE AND F. BAERTZ. *Sucr. Belge* 44, 414-31(1925).—The effects of variation in liming and carbonating were investigated. Ordinary liming in 2 stages does not give as good results as liming in a single stage. A series of expts. is reported which indicate that double flocculation may be of considerable importance, in that the samples that had undergone the double flocculation all showed a notable gain in purity. Numerous expts. were made on the rates of filtration of juice limed in various ways. In general the rate of filtration decreases as the quantity of lime added to the juice is increased from 0.2 to 1.0%. The authors believe that at present the beet-sugar factories are not equipped to take advantage of the marked increase in purity obtained by the double flocculation.  
T. M.

The Genter thickener. A. MARION *Sucr. Belge* 44, 449-55(1925).—A description of the development of the Genter thickener with diagrams illustrating the constructive features. M. gives extensive data or results obtained during the 1924-1925 campaign in 2 American sugar factories. In these factories the slimes from the second carbonation are filtered off by means of Kelly presses and after mixing with the first carbonation sepd. by the Genter thickener, are sent to the Oliver filters, for the performance of which data are also given.  
T. MARKOVITS

Crusher-shredder. F. MAXWELL. *Facts About Sugar* 20, 663-4(1925).—There is a marked advance in the mill treatment of sugar cane so that the cane is prepd. in the first mill increasing the extn.  
T. MARKOVITS

Electrical equipment in the sugar mill. E. B. SMITH. *Facts About Sugar* 20, 615-7(1925).  
T. MARKOVITS

The development of the Elfa apparatus from the hydraulic conveyor in beet-sugar factories. K. FÖLSCH. *Chem. App.* 12, 95-7, 105-7, 124-5(1925).—Description with 15 cuts.  
J. H. MOORE

Corrosion—its cost and prevention. R. B. WILLIAMS. *Facts About Sugar* 20, 472-3(1925).—W. gives methods by which corrosion can be eliminated from sugar-house equipment. The system of water treatment and soil corrosion of pipes are discussed.  
T. MARKOVITS

Sugar-cane experiments. J. S. DASH. *Trop. Agr. (Trinidad)* 2, 123-4(1925).—The yield of sugar per acre was much larger from fall-planted canes than from those planted in the spring. However, the % of sucrose in the juice was about the same in both lots. Chem. data on a no. of varieties planted under different conditions are presented in tabular form.  
A. L. MEHRING

Handling cane tassels for breeding work. J. A. VERRET. *Facts About Sugar* 20,

638-40(1925).—A description of the use of  $H_2SO_4$  soln. for preventing losses of cuttings during transfer and test periods. T. MARKOVITS

The cane borer in Java. S. N. QUAR. *Facts About Sugar* 20, 662-3(1925).—Proper care of the crop and selection of varieties making heavy growth hold ravages of pest in check. T. MARKOVITS

The specificity of starches. R. CHODAT with the collaboration of J. W. ROSS AND M. PHILIA. *Compt rend des séances soc. phys. hist. nat. Genève* 41, 122-6(1920); *Physiol. Abstracts* 9, 557—Apart from microscopic differences, starches from various sources have been shown to exhibit different behavior during diastatic action, leading to the conclusion that there are differences in the degree of polymerization in the "amylose" and "amylopectin" present. H. G.

Annual report of the agricultural chemist to government, Punjab (LANDER) 15.

DOWLING, R. N.: *Sugar Beet from Field to Factory*. Foreword by Daniel Hall. London: Benn Brothers 72 pp. 2s. 6d.

Treating sugar juices. J. C. HEDDEN. U. S. 1,545,321, July 7. Nitrogenous substances are pptd. from cane juice and the ppt. is treated with  $Al_2(SO_4)_3$  or other salt of a metal which when decomposed with alkali will form an insol. hydroxide, and tannic acid is then added, to form a purifying reagent.

Purifying sugar solutions. J. C. HEDDEN. U. S. 1,545,318, July 7. Sugar juices, sirups or other solns. are treated with a substrate carrying pptd.  $Al(OH)_3$  or other dye-mordant which is insol. in  $H_2O$  and will fix basic coloring substances and take up mordant coloring substances. Cf. following pats.

Purifying sugar juices. J. C. HEDDEN. U. S. 1,545,319, July 7. The juice is treated with  $CaCO_3$  or other carbonate which is substantially insol. in the juice to neutralize acids in the juice which are "stronger than"  $CO_2$  and the treated juice subsequently is submitted to the action of another reagent, e. g., hydroxide of Fe or Al (pptd. on hagsasse), which will neutralize acids weaker than  $CO_2$ . Cf. preceding pat.

Regenerating sugar-purifying reagents. J. C. HEDDEN. U. S. 1,545,320, July 7. In regenerating tannin compds. or other basic activated compds. insol. in  $H_2O$ , which have been used for purifying cane sugar juices, the impurities taken up by the activated substance are hydrolyzed, e. g., by heating with  $H_2O$  and an acid or salt, and are then washed out of the material. Cf. following pat.

Regenerating sugar-purifying reagents. J. C. HEDDEN. U. S. 1,545,322, July 7. A spent activated mordant substance such as a basic tannin compd. which has been used for purifying sugar juices or solns. is regenerated by treatment with an alkali soln., e. g.,  $NaOH$ , which will decompose and render sol. the impurities present.  $H_2O_2$  also may be used as an oxidizing agent. Cf. preceding pat.

Crystalline glucose. CORN PRODUCTS REFINING CO. Brit. 227,140, July 12, 1923. In producing cryst. glucose of a regulated degree of hydration, a concd. soln. is cooled to a temp. suitable for production of crystals of the type desired and seeded with crystals of that type, agitated while crystn. takes place and the crystals are sepd. centrifugally. Hydrated crystals are produced from a 40° Bx. soln. at a temp. of about 35-40° and anhyd. crystals with the use of a slightly higher concn. and temp.

## 29—LEATHER AND GLUE

ALLEN ROGERS

Mechanism of tanning processes. V. Diverse views on the theory of tanning and conclusions therefrom. G. POVARNIN. *Collegium* 1925, 287-304; cf. C. A. 18, 3488. —A review of the theories of tanning and tawing. I. D. CLARKE

Chrome tanning. I. Tanning and nontanning chrome complexes. E. STIASNY, K. LOCHMANN AND E. MEZEY. *Collegium* 1925, 190-200—Cr compds. of 4 types were prepd. and were found by tests on hide powder and pieces of skin to be of no value for tanning. The 4 types of compds. were compds. in which the Cr was present in (1) a complex anion, (2) a complex cation which contains no  $H_2O$ , (3) an uncharged complex, and (4) a complex cation which contains  $H_2O$  and which does not hydrolyze in  $H_2O$  soln. II. The relation between direction of migration and tanning action. E.

STIASNY AND K. LOCHMANN. *Ibid* 200-7.—Diln. and aging favor the formation of complex cations. There was no relation between the direction of migration and ability to tan. The compn. and stability of the Cr complex are of more importance than its charge.

I. D. CLARKE

Fixation of constituents of chrome liquors by hide substance from highly concentrated chrome solutions. K. H. GUSTAVSON. *Ind. Eng. Chem.* 17, 823-6(1925); cf. C. A. 19, 1961.—By plotting the amt. of Cr fixed by hide substance under uniform conditions against the concn. of basic chrome liquor, in g.  $\text{Cr}_2\text{O}_3$  per l., a curve is obtained showing a max. at 17, a min at 120, a second max. at 140, a min. at 180, and a third max. at 193, followed by a decline. The concd. liquors contain Cr complexes some of which are positively and some negatively charged. The primary chem. reaction between Cr ion and collagen is complicated by the co-pptn. of oppositely charged Cr complex and collagen. The results can only be explained on the basis of a chem. conception of chrome tanning.

J. A. WILSON

Report of the meeting of German leather chemists in Darmstadt, March 18, 1925. *Collegium* 1925, 270-4.—A discussion on Cr tanning. Cr liquors in which the Cr is in a complex anion will produce a fine-grained and probably valuable leather. An app. is described for detg. the "pptn. point" of Cr liquors. A beam of light is directed through a hole in the bottom of a black box and into the beakers contg. the soln. NaOH is added until a distinct Tyndall cone is observed.

I. D. CLARKE

Tanning with concentrated chrome solutions. J. BERGMANN. *Collegium* 1925, 174-87.—Contrary to statements of Schorlemmer (C. A. 17, 2062), the Cr salt taken up in "dry tanning" is less basic than the salt in the original soln. The greater the concn. of the liquor, the more acid the salt which is fixed by the skin and the more nearly the bath is exhausted. A 20° Bé. liquor, 61% basicity, was 95.7% exhausted; from more basic liquors less Cr was taken up probably because part of the Cr had entered into a non-tanning complex anion. For dry tanning, all ordinary exts. and concns. other than 20° Bé. can be used. The dry-tanned leather was grisly and wrinkly but a little NaCl in the bath changed the properties considerably, making the leather more like that tanned by the usual method.

I. D. CLARKE

Tanning materials from Travancore. ANON. *Bull. Imp. Inst.* 23, 158-68(1925).—Samples of bark of "Elengi" (*Azimusops elengi*, L.) (No. 1, No. 9), "Perszhu" (*Careya arborea*, Roxb.) (No. 2, No. 10), "Mora" or "Munga perszhu" (*Buchanania latifolia*, Roxb.) (No. 3), "Vaga" (*Albizia lebbek*, Benth.) (No. 4, No. 11), "Karrencha" (*Acacia pennata*, Willd.) (No. 5, No. 12), "Thambagom" (*Hopsea parviflora*, Bedd.) (No. 6), "Venga" (*Pterocarpus marsupium*, Roxb.) (No. 7) and "Thembavu" (*Terminalia tomentosa*, Bedd.) (No. 8) were analyzed with the following results:

Sample number	$\text{H}_2\text{O}$	Insol.	Extractive matter (Non-tannin)		Ash	Tintometer Red	readings	
			Tannin				Yellow	
1	10.7	74.3	10.5	4.5	2.9			
2	9.9	73.7	6.2	10.2	6.0	23.7	42.5	
3	8.7	68.5	9.4	13.4	11.9	16.2	30.0	
4	10.4	68.5	15.8	5.3	4.3			
5	10.4	77.2	9.4	3.0	4.7			
6	9.8	68.2	9.7	12.3	2.2	3.5	9.4	
7	9.9	73.0	12.9	4.2	9.6	76.8	168.0	
8	11.4	64.0	4.4	20.2	6.7	24.6	28.7	
9	13.1	75.1	8.5	3.3	4.1	70	200	
10	11.3	65.5	5.1	18.0	5.6	17.3	35.5	
11	12.7	79.5	5.9	1.9	3.7	43.8	76.9	
12	14.1	71.8	4.9	9.2	3.9	13.4	24.4	

None of these would be suitable for export as such, but Nos. 6, 8 and 10 would be suitable for the manuf. of ext.

A. PAPINEAU-COUTURE

Variation of strength and stretch over the area of calf leather. J. A. WILSON. *Ind. Eng. Chem.* 17, 829-30(1925).—A chart and curves showing the relation of tensile strength and tendency to stretch under a fixed load to the location on the skin of typical, finished calf leather.

J. A. WILSON

Measurement of the porosity of leather. A. REISNER. *Westnick, Bolet des Allruss Ledersyndikats* No. 6-8, 32 pp.(1923); *Collegium* 1925, 165-7.—The porosity was measured by immersing the leather in a known vol. of a solvent which would wet the leather ( $\text{H}_2\text{O}$ ,  $\text{CCl}_4$ , mineral oil, etc.) and noting the decrease in vol. The porosity of sole leather

was 20-50%. H<sub>2</sub>O did not always fill all the pores, it caused a swelling of 10-30%. Leather stuffed wet has about 8% greater vol. than ungreated leather. I. D. C.

Volumetric method for determining the ability of sole leather to take up water. A. REISNER *Wesnik, Bole des Allruss Ledersyndikats* No. 9, 17 pp (1923); *Collegium* 1925, 187-8.—The increase in wt. of leather in H<sub>2</sub>O less the porosity gives the mol. H<sub>2</sub>O absorption. The max. total H<sub>2</sub>O absorption should be not over 35% and the mol. imbibition not over 15% for good sole leather. The d. of the leather fibers was approx. const. and between 1.4 and 1.47. I. D. CLARKE

Preparation of hide powder for analysis. L. MEUNIER AND P. CHAMBERD. *J. Soc. Leather Trades Chem* 9, 23-6 (1925).—See C. A. 19, 747. E. J. C.

Manufacture of quebracho extract. R. O. PHILLIPS *Chem. Met. Eng.* 32, 611-4 (1925). E. H.

The fluorescence of fisetin with Wood's lamp; applications. LOUIS MEUNIER, *Cuir tech.* 14, 251-2 (1925).—Many fibrous materials, impregnated with quebracho, show a strong yellow fluorescence by reflected light from Wood's lamp. This behavior, attributed to fisetin, may be used to distinguish quebracho from other tannin materials. H. B. MERRILL

The limits of precipitability of gelatin by tannin. J. A. SMORODINTZEV AND A. N. ANOVA *Z. physiol. Chem.* 144, 255-8 (1925).—Aq. solns. of gelatin at  $p_H$  4.91 are pptd. at greater diln. by tannin than at  $p_H$  8.95-10.06. Tannin solns. contg. NaCl give more distinct pptn. At  $p_H$  10.06 a 0.25% gelatin soln. is not pptd. by tannin, nor at neutrality if the gelatin concn. is less than 0.003%. A concn. of less than 0.013% gives no ppt. at  $p_H$  8.95. A. W. DOX

Purification of tannery sewage by sulfur dioxide. U. J. THUVAU AND LUCIEN FAYRE. *J. Soc. Leather Trades Chem* 9, 39-41 (1925).—See C. A. 19, 747. E. J. C.

Impregnating fabrics with wax (Brit. pat. 227,188) 25.

Leather-like fabric. W. E. GWALTNEY. U. S. 1,544,744, July 7. A tough, pliable material is made by subjecting a bat of interlaced cellulose fibers, e. g., cotton or ramie, to the action of a soln. such as xanthate or viscose which exerts a solvent action on the fibers without destroying their structure, and then impregnating the resulting sheet with an insol. colloidal binder such as a glue compn. which may be tanned in the material.

Leather from shark skins and similar substances. K. BENEDIXEN and ALFRED ENGENREICH *Danish* 34,285, March 16, 1925. The thorns and horny plates in the epidermis of the skins are loosened by chem. means, the skins are tanned with vegetable or other org. tanning materials and then treated with an aq. acid soln., after which the thorns and horny plates may be removed by a gentle mech. working.

### 30—RUBBER AND ALLIED SUBSTANCES

C. C. DAVIS

The value of the chemist in the rubber industry. ANON. *Gummi-Ztg* 39, 1613-4 (1925). C. C. DAVIS

Heat of combustion of natural and "sulfuric acid" rubber. F. KIRCHHOF AND O. MATULKE *Ber.* 57B, 1266-70 (1924).—The heat of combustion of plantation pale crepe rubber is approx. 10,700 cal. per g. The empirical formula is  $(C_{11}H_{14})_n$ , and is therefore identical with that of Congo rubber and synthetic isoprene rubber. The heat of combustion of "sulfuric acid" rubber (Kirchhof, C. A. 15, 961; 16, 1885) is markedly lower than that of natural rubber and depends on the degree of internal polymerization. Its empirical formula, calcd. to material free from ash and sulfate, corresponds closely to  $(C_{10}H_{12}SO_2)_n$ . The action of H<sub>2</sub>SO<sub>4</sub> on resin-free natural rubber in different media is accompanied by an evolution of heat which is approx. proportional in amt. to the content of undissolved rubber; the latter is partially depolymerized and oxidized. The transformation (internal polymerization) is however attended by absorption of heat. B. C. A.

The constitution of the rubber molecule. S. C. J. OLIVIER. *Rec. trav. chim.* 44, 229-38 (1925).—A discussion of the work of Harries (C. A. 9, 233), H. and Evers (C. A. 16, 3232), Boswell (C. A. 17, 2655), Staudinger and Fritzsche (C. A. 17, 2974),

Pummerer and Burkard (C. A. 17, 898) and Kirchhof and Matulke (cf. preceding abstr.). O concludes that although the open-chain formula seems most acceptable the problem has not yet been solved. The latter is complicated by the fact that there is no evidence that rubber, an amorphous colloidal substance, is not a mixt. E. J. WITZEMANN

What are the reasons for the characteristic elasticity of rubber? I. The changing of the X-ray spectrum of rubber on stretching. J. R. KARY. *Kolloid-Z.* 36, 300-7 (1925)—It has already been shown (C. A. 19, 2144) that rubber on being stretched acquires a cryst. structure and that highly stretched rubber consists largely of crystals which lie parallel to the direction of elongation. The lattice space in the direction of the stretching is 8 Å. U., which indicates that the mols. are composed of units each of which acts as a center or cell for producing the interference diagram, for 8 Å. U. is less than the probable diam. of a single mol. Unvulcanized rubber requires less stretching than vulcanized rubber to show the X ray diagram characteristic of a cryst. substance. The first stretching of rubber is due to the rearrangement of these structural units in the mol. Other gel-like substances with little fluidity but a Poisson const. near to 0.5 must also show strong tendencies to stretch. F. E. BROWN

Improvement of the tone of fiber strings by latex or by solvol. RUDOLF DITMAR. *Gummi Ztg.* 39, 1682(1925)—Cord composed of silk, wool, hemp or other fiber can be improved in strength and in durability by impregnating it with rubber latex. When used for violin strings not only can the appearance of catgut be imitated but the tone of the instrument is much improved. The cord is first impregnated with rubber by immersing it in latex, which may also contain a little glycerol and a reducing agent like hydroquinol. When dry it is coated with spermaceti or with hard paraffin and finally with soapstone or with a luster varnish. The process may be modified by adding S to the latex, in which case the cord is vulcanized before the final protective coating is applied. Similarly cord may be treated with solus of rubber in org. solvents and vulcanized so that it is suitable for use in rackets, chairs, etc. Excellent results are also obtained with "solvol" in place of latex. See German Patents 19,240, Class 73, 62,246 Class 73, 117,305, 125,748, 326,335, Austrian Patent 74,065. C. C. DAVIS

Effect of zinc white and magnesium carbonate on the physical properties of vulcanized rubber. Y. FUKUI. *Report Osaka Ind. Research Lab.* 5, No. 5, 1-24(1924)—Mixts. of smoked sheets 100 and S 10 contg. 5-300 parts of ZnO or 1-100 parts of MgCO<sub>3</sub> were tested, after curing 30-240 min. at 40 lbs. steam pressure, for elasticity, tensile strength, compressibility and durability. The results show that a small amt. of ZnO reduces all of these properties, whereas MgCO<sub>3</sub> improves them. The best quality in general was obtained with 60-200 parts of ZnO and with 3-80 parts of MgCO<sub>3</sub>. The latter was particularly valuable for its reinforcing power and at the same time accelerated the cure, whereas ZnO was most valuable as a white pigment, but retarded the cure. The ZnO was Pb-free, the MgCO<sub>3</sub> impure (86.98% loss on ignition). These 2 pigments are used most extensively in Japan. S. T.

Fuel for portable vulcanizers (Brit. pat. 227,717) 21. Rubber-faced wall coverings (Brit. pat. 227,578) 20. Rubber-faced tiles, building blocks, etc. (Brit. pat. 227,153) 20.

Chlorinated rubber. C. ELLIS. U. S. 1,544,529, June 30. Rubber is masticated with a volatile solvent softening agent such as C<sub>6</sub>H<sub>6</sub>, toluene or solvent naphtha and agitated in an atm. of Cl<sub>2</sub>. U. S. 1,544,530 specifies treating fragments of unvulcanized rubber with Cl<sub>2</sub> and dissolving away the chlorinated rubber from the fragments so that a sponge like product is formed. U. S. 1,544,531 (C. ELLIS and N. BOEHMER) specifies exposing rubber to the action of Cl<sub>2</sub> under pressure in excess of combining requirements and at an elevated (but non charring) temp., e. g., about 70°. U. S. 1,544,532 (C. ELLIS) specifies incorporating more unvulcanized rubber in a bulk of CCl<sub>4</sub> or other solvent than could be dissolved by the latter, and agitating the materials at a temp. above room temp. but below the b. p. of the solvent. U. S. 1,544,533 specifies exposing unchlorinated rubber under pressure to spent Cl<sub>2</sub> gas contg. HCl. U. S. 1,544,534 (C. ELLIS and N. BOEHMER) specifies reacting with Cl<sub>2</sub> gas under pressure on loosely packed pieces of rubber freely permeable to the circulating Cl<sub>2</sub> and thus exposing the rubber to cause an exothermic reaction and consolidate the pieces into a coherent mass of highly chlorinated rubber. The chlorination chamber is vented intermittently to remove HCl. U. S. 1,544,535 specifies chlorinated rubber contg. free Cl which serves as a plasticizing agent.

Rubber from latex. C. C. LOOKIS and H. E. STUMP. U. S. 1,543,932, June 30. S in colloidal form is introduced into a natural latex, and the latter is then vulcanized.

**Forming rubber articles from latex.** E. HOPKINSON and W. A. GIBBONS. U. S. 1,545,257, July 7. In making threads, tubing, strips or similar articles, a solid mass of rubber is formed from a stream of latex continuous with the latter. Cf. C. A. 19, 2425.

**Curing rubber.** R. B. STRINGFIELD. U. S. 1,544,699, July 7. An inorg. oxide gel such as silica gel is used as a carrying agent for  $H_2S$  and  $SO_2$  or other compounding fluids for rubber.

**Vulcanization accelerators.** L. B. SENRELL and C. W. BEDFORD. U. S. 1,544,687, July 7. Rubber vulcanization is accelerated by the use of mercaptobenzothiazole (or its Pb or Zn salts) and benzothiazyl disulfide polysulfide. U. S. 1,544,688 specifies the use of a Pb salt of mercaptobenzothiazole as an accelerator.

**Handling carbon dioxide or other non-oxidizing gases in the vulcanization of rubber.** H. R. MINOR. U. S. 1,544,023, June 30. Mech. features.

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SEPTEMBER 20, 1925

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# CHEMICAL ABSTRACTS

Vol. 19.

SEPTEMBER 20, 1925

No. 18

## 1—APPARATUS AND PLANT EQUIPMENT

W. L. BADGER

A distillation flask for corrosive liquids. F. E. BROWN. *Ind Eng Chem* 17, 706(1925) E. H.

An apparatus for measuring the optical constants of crystals in the ultra-violet. PIERRE SÈVE. *Compt. rend* 180, 1951-2(1925).—An arrangement consisting of a carbon arc and a system of quartz lenses is used in studying birefringence and the angle between optical axes of crystals by photographic means down to 2400 Å. U. R. J. H.

Gas-absorption pipet. A. O. JONES. *J Soc Chem Ind* 44, 115-6T(1925).—An inexpensive and convenient form of app. is described. T. S. CARSWELL.

A semi-automatic filling pipet for the delivery of constant volumes of reagent. V. B. CONNELL. *Ind Chemist* 1, 276(1925) E. H.

Electrode vessel for liquids heavier and lighter than the liquid junction potential eliminator. L. E. DAWSON. *J. Am. Chem. Soc* 47, 2172-3(1925).—The apparatus is more durable and less expensive and intricate than that employed hitherto. H. C. P.

A practical design of a hydrogen electrode. F. VLÈS AND E. VELLINGER. *Bull. soc. chim.* 37, 771-2(1925).—Illustrated description of a design of H electrode particularly suited for the detn. of H-ion concn. in semi-plastic solids. The electrode is also well suited for ordinary H-ion concn. detns. The H electrode proper is mounted above and in one piece with a calomel electrode, the two parts being connected with a tube of satd. KCl soln. The liquid in the H electrode can be easily removed and the electrode cleaned. R. L. DODGE.

Sensibility of actinometers with electrodes of silver iodide and copper oxide. G. ATHANASIC. *Compt. rend.* 181, 101-3(1925), cf. *C. A.* 19, 1336.—The Ag electrodes were prepd electrolytically. The CuO electrodes were prepd. by heating without contact with the flame, by heating directly in the flame, or by heating and plunging into CH<sub>3</sub>OH. The results for Ag are given for the range  $\lambda = 5460$  Å. U. to  $\lambda = 2536$  Å. U. The max. sensibility was found at  $\lambda = 4245 \pm 20$  Å. U. For Cu the sensibility showed a max. for  $\lambda = 4046$  Å. U. and a min. for  $\lambda = 3100$  Å. U. These were independent of the method of oxidation and of the electrolyte employed. W. W. STIFLER.

Removal of sulfur chloride and similar liquids from carboys. RALPH DEFRIE. *Chemistry & Industry* 44, 615-6(1925).—A bottle is fitted with a rubber stopper carrying two pieces of glass tubing bent at right angles, over the ends of which are rubber connecting tubes provided with screw clamps. The bottle is evacuated with a filter pump, then connected with a long tube dipping into the liquid in the carboy, the clamp opened, and the liquid allowed to flow into the bottle. A cork bung carrying a glass tube reaching to the bottom of the carboy, and a shorter one acting as an air inlet, may be used in the carboy. W. C. EBARTH.

GOODWIN, H. Autoclaves and High Pressure Work. London: E. Benn, Ltd 166 pp., 6s.

Apparatus for spray evaporation of solutions, emulsions and suspensions. F. WREESMANN. *Brit.* 228,747, April 14, 1924.

Apparatus with tubular preheater and vertical calandria for evaporating liquids. A. BLAIR and BLAIR, CAMPBELL & McLEAN, LTD. *Brit* 228,691, Jan. 12, 1924.

"Continuous" circular hearth furnace. T. F. BAILY and F. T. COPE. U. S. 1,546,703, July 21.

Kiln for heating, drying or coking coal, ores, bituminous slate, etc. O. DOBBELSTEIN and H. HESS. *Brit.* 228,532, Feb. 2, 1924.

Filtering apparatus for raw oils or other liquids. P. DEBNE. U. S. 1,547,368, July 28.

- Portable filter for water or other liquids. W. E. DUNBAR. U. S. 1,547,105, July 21
- Filter J. C. BETTERIDGE and H. J. COX. Brit. 228,624, Nov. 7, 1923. A cylindrical filter basket can be rotated for cleaning by a brush or scraper mounted adjacent to it.
- Apparatus for separating oil from water, etc. F. C. HAMILTON. U. S. 1,546,655, July 21
- Apparatus for separating constituents of air or other mixed gases under the action of a magnetic field. D. DOW, E. P. LOVEJOY and T. J. CASE. U. S. 1,546,632, July 21.
- Thermostat for controlling gas flow to burners. A. L. H. SPENCER and SPENCER-BONECOURT, LTD. Brit. 228,652, Nov. 14, 1923
- Burner for solid metaldehyde and similar substances. A. BUSCH. U. S. 1,547,200, July 28.
- Device for recording specific gravity of oil or other liquids flowing through the apparatus. E. G. BAILEY. U. S. 1,546,702, July 21
- Röntgen-ray apparatus. AKT.-GES. FÜR ANILIN-FABRIKATION, Brit. 228,270, Nov. 6, 1923
- Röntgen-ray apparatus. H. S. SAWFORD. Brit. 228,533, Jan. 26, 1924.
- Grid for X-ray photography. E. S. FLAARHEIM and J. G. H. LIEBEL. U. S. 1,547,376, July 28. Parallel strips of wood and Pb or other materials permeable and impermeable, resp., to Röntgen rays, are secured together side by side in alternate arrangement.
- Filaments for thermionic tubes, etc. W. R. BULLIMORE. U. S. 1,546,776, July 21. Wire or a C filament is coated with celluloid or other agglutinant, passed through a solvent for the agglutinant, e. g.,  $\text{AmOAc}$ , to render the surface tacky, and then coated with an electron-emitting material, e. g., an alk. earth metal oxide.
- Apparatus for concentrating fruit juices or other solutions by freezing. E. MONTE. U. S. 1,546,669, July 21
- Apparatus for sterilizing air for use in treating or storing foods, etc. J. A. LINLEY. Brit. 228,521, Feb. 1, 1924. The app. comprises tanks for  $\text{CaCl}_2$ ,  $\text{CH}_2\text{O}$ ,  $\text{H}_2\text{SO}_4$  or other substances for treating the air, which may also be heated.

## 2—GENERAL AND PHYSICAL CHEMISTRY

GEORGE L. CLARK AND BRIAN MEAD

- New light on phlogiston. T. L. DAVIS. *Chemistry & Industry* 44, 725-7(1925) — Historical. H. H.
- The method of proportional differences for the simplification of calculations. G. BRUHNS. *Chem.-Ztg.* 49, 528-9(1925).—By numerical problems the method of applying proportional parts or differences to numerical examples is explained and recommended. W. C. EBAUGH
- The classification of atoms. A. W. SYEWAAT. *Scientia* 37, 373-82(1925).—Elementary consideration of the periodic system, emphasizing valence in terms of cohesion. G. L. CLARK
- A system of the chemical elements and isotopes. S. A. SHCHUKAREV. *J. Russ. Phys.-Chem. Soc.* 55, 447-76(1924).—The elements and isotopes are classified into 4 groups, characterized by the at. masses of the generic formulas  $4n + 2$ ,  $4n + 1$ ,  $4n$ ,  $4n - 1$ . The members of either of them may be connected to genealogical series, which comply with the laws of Soddy and Fajans, and Meitner's rule, just like  $\alpha$  and  $\beta$  emanations of the radioactive series. The elements of the even groups 0, II, IV, VI, VIII (with exception of Co, Rh, Ir) have even atomic nos., even no. of nuclear charges, mostly even at. wts., and mainly even valences. The elements of the odd groups and the central members of the triads of group VIII are characterized by odd at. nos., etc. The structural units of the nuclei are considered to be  $\alpha$  or  $(\alpha + 2\beta)$  particles. To account for the expulsion of  $\beta$  particles only, the existence of special nuclear groups, e. g.,  $\beta_{\text{pe}}$ ,  $\beta_{\text{pe}}$ ,  $\beta_{\text{pe}}$  ( $\beta$  = proton,  $e$  = electron) is anticipated. The genealogical series of the group  $4n$  is characterized by the general formula:  $(2\alpha + \alpha\beta\beta) + [(9\alpha + 3\alpha\beta\beta) + (7\alpha + 3\alpha\beta\beta)] + (9\alpha + 3\alpha\beta\beta) + (9\alpha + 3\alpha\beta\beta) + 1\alpha + 1\alpha$ . The one of the group  $4n + 2$  by the formula:  $(3\alpha + \alpha\beta\beta) + [(9\alpha + 3\alpha\beta\beta) + (7\alpha + 3\alpha\beta\beta)] + (9\alpha + 3\alpha\beta\beta) + (9\alpha + 3\alpha\beta\beta) + 4\alpha + (3\alpha + \beta)$ . The first and third odd isobars cannot be observed in mass spectrographs, the second one is visible. The first and third even isobars are visible, the second not. Genealogical tables of the elements and of the isotopes of 1st order (the 2 most important ones) and of the second order (the other observable isotopes)

are given, well illustrating the ideas brought forth. A certain periodicity reveals itself, if the log of occurrence of the elements is plotted against the corresponding at. wts., grouping separately even and uneven elements, these logs decrease with increasing at. wts., the decrease in the odd series being about 1.5 times as large as in the even one; this is in conformity with the stability of the corresponding nuclei. The nuclei of the odd series are probably less stable because of the groups  $ps_2$ , etc., present. The relative stability of the unstable heavy nuclei is explained by the relatively negative character of the nuclei  $4n + 1$  and  $4n + 2$ . Light nuclei are characterized by  $4n - 1$  and  $4n$ . In the central part of the system all four groups being equiv., the largest no. of isotopes is to be found. The rare occurrence of Sc and Ga is due to the unstable structure of their atoms, of the formula  $4n + 1$ . The odd elements are represented by one isotope, if there are corresponding  $\alpha$  transformations in both genealogical families ( $4n - 1$  and  $4n + 1$ ), by two isotopes if an  $\alpha\beta\beta$  transformation occurs in either of both families. The one with the smaller mass is present in a larger amt. A certain periodicity is observed in the genealogical series of the individual groups. It is shown that the relative amt. of the isotopes in a given pleiad can be explained by Fajans' rule. H. B.

Revision of the compressibility of methyl chloride and the molecular weight of this gas. T. BATUECAS. *Compt rend* 181, 40-2 (1925).—By means of the same method and app. as were used for  $\text{Me}_2\text{O}$  (C. A. 17, 3118) the deviation factor  $(1 - \lambda)$  for Avogadro's law was found to be 1.0247. The deviation of the compressibility becomes 0.0241 instead of 0.02215 as found by Baume (C. A. 2, 1519). The calcd mol. wt. is 50.193, corresponding to  $\text{Cl} = 35.470$ . A. W. FRANCIS

The hydrate of xenon. DE FORCRAND. *Compt rend* 181, 15-7 (1925), cf. C. A. 17, 1390.—Analogous to those of Kr and Ar, a cryst. hydrate of Xe with 6 or  $7\text{H}_2\text{O}$  was obtained by cooling under moderate pressure. The critical dissociation temp. is  $24^\circ$  compared to  $13^\circ$  for Kr  $5\text{H}_2\text{O}$ . The dissociation pressures at  $0^\circ$  for hydrates are Xe 1.4, Kr 14.5, Ar 93.5 atm. A. W. FRANCIS

The reflection of X-rays by rock salt. J. A. WASASTJERNA. *Soc. Scient. Fennica Comm. Phys.-Math.* 2, No. 15, 1-25 (1925).—The intensity of reflection of Mo K $\alpha$  X-rays from the 100 face of rock salt is measured in a manner rather similar to that of Bragg, James and Bosanquet (C. A. 15, 1453, 2786). The integrated reflection and coeff. of extinction are calcd. By the use of diaphragm arrangements, the power reflected at various depths from the crystal surface is measured and the actual coeff. of absorption ( $\mu = \mu_0 + \epsilon$ ) is calculated directly. The value of  $\epsilon$  is found to be 4.4, in fair agreement with the value indirectly obtained by Bragg, James and Bosanquet. The reflecting power varies with the depth in the crystal of the reflecting element. R. J. H.

Crystal structure of the mercurous halides. R. J. HAVIGHURST. *Am. J. Sci.* 10, 15-28 (1925).— $\text{Hg}_2\text{Cl}_2$ ,  $\text{Hg}_2\text{Br}_2$  and  $\text{Hg}_2\text{I}_2$  are shown by the powdered-crystal method of X-ray analysis to possess similar crystal structures. Reflections of the tungsten K-series from single crystal faces of calomel confirm the choice of the unit cell for  $\text{Hg}_2\text{Cl}_2$ . The crystal structure is detd. with the help of the theory of space-groups. The unit cell contains 2 mols. of  $\text{Hg}_2\text{H}_2$  and has the following dimensions:  $c \approx 10.89$ , 11.10, 11.61 Å. U. and  $a = 4.47$ , 4.65, 4.92 Å. U. for  $\text{Hg}_2\text{Cl}_2$ ,  $\text{Hg}_2\text{Br}_2$  and  $\text{Hg}_2\text{I}_2$ , resp. The X and Y axes differ from those in ordinary crystallographic use by a rotation through  $45^\circ$  about the Z axis. Hg atoms are located at  $00u$ ;  $00\bar{u}$ ;  $\frac{1}{2}\frac{1}{2}\frac{1}{2}(\frac{1}{2}-u)$ ;  $\frac{1}{2}\frac{1}{2}\frac{1}{2}(\frac{1}{2}+u)$ ; and Hl atoms are at  $00v$ ;  $00\bar{v}$ ;  $\frac{1}{2}\frac{1}{2}\frac{1}{2}(\frac{1}{2}-v)$ ;  $\frac{1}{2}\frac{1}{2}\frac{1}{2}(\frac{1}{2}+v)$ . Values of  $u$  are 0.110, 0.108, 0.103; and for  $v$ , 0.360, 0.358, 0.355, for  $\text{Hg}_2\text{Cl}_2$ ,  $\text{Hg}_2\text{Br}_2$  and  $\text{Hg}_2\text{I}_2$ , resp. The structure proposed by Mauguin (C. A. 18, 2447), for calomel is similar to this, but does not require a parameter. The strong positive double refraction of the mercurous halides is to be expected from this structure. The existence of a chain molecule,  $\text{Hl}-\text{Hl}-\text{Hl}$ , in the crystal is indicated. R. J. H.

Iron hydrates and iron oxide. A. SIMON AND T. SCHMIDT. *Kolloid. Z. Spec. Na.* 65-80 (Apr. 1, 1923).—Three hydrated oxides of Fe were prepd. by: (1) pptn. of the gel by adding  $\text{NH}_4\text{OH}$  to a cold soln. of  $\text{FeCl}_3$ , (2) pptn. at  $40^\circ$  by adding  $\text{NH}_4\text{OH}$  to pure  $\text{Fe}(\text{NO}_3)_3$  and washing by decantation until free from  $\text{NH}_4\text{NO}_3$ ; (3) dialysis in the dialyzer designed by Cutbier of the pure  $\text{Fe}(\text{NO}_3)_3$  used in (2) for 14 days or until no  $\text{NO}_4^-$  ion was present. The  $\text{Cl}^-$  ion could not be completely removed from (1). (3) was very fine, (2) very coarse and (1) was of intermediate fineness. All were kept in a moist condition. All the decomposition diagrams obtained from these hydrates were continuous curves and gave no indication of the existence of definite hydrates contg. 1, 2, or more  $\text{H}_2\text{O}$  (cf. Willstätter and Kraut, C. A. 18, 2090). The amt. of  $\text{H}_2\text{O}$  contained was in the order (2) < (1) < (3). The  $\text{H}_2\text{O}$  was held more firmly by (3) than by (2) as shown by the fact that at  $130^\circ$  (2) still contained 0.65  $\text{H}_2\text{O}$  and (3) 1.23  $\text{H}_2\text{O}$ . The vapor-pressure curve of (2) appeared to follow the equation  $\ln P_0/P = k/n$ , i. e., to

satisfy the conditions for a completely amorphous system with capillaries whose diams. are of mol size. As shown by X-ray crystallography the air-dried hydrated oxide (2) was completely amorphous, the  $H_2O$ -free oxide (2) was cryst., though amicroscopic. The air-dried (3) was cryst. though the value for the lattice const. varied from the usual value for  $Fe_2O_3$  and the characteristic lines were not distinct. This indicates that more or less  $H_2O$  lies between the oriented  $Fe_2O_3$  mols. in the lattice. It is possible that with time, and when aided by heat, more  $H_2O$  mols. gradually assume fixed positions in the  $Fe_2O_3$  lattice, until finally a stoichiometrical relation exists between the  $Fe_2O_3$  and the  $H_2O$  (cf. Wedekind *C. A.* 18, 1772, and Hüttig, *C. A.* 19, 1364). The pure  $Fe_2O_3$  was prepd. by heating (2) to const. wt. at  $700^\circ$ . The decompn. curve (isobar) proved the existence of 2 definite chem. individuals,  $Fe_2O_3$  and  $Fe_3O_4$ . The transition occurred at  $1300-20^\circ$ . The  $Fe_2O_3$  gave very many interference lines which indicated a complicated structure whose arrangement is still unknown. The prepn.  $FeO$  gave lines side by side of almost equal strength corresponding to  $Fe_2O_3$  and  $Fe_3O_4$ . No other lines were found. Therefore both compds. occur together, though neither as mixed crystals nor as intermediate oxides.

H. M. McLAUGHLIN

The crystal structure of lithium potassium sulfate. A. J. BRADLEY, *Phil Mag* 49, 1225-37 (1925).—The cryst. structure of  $LiKSO_4$  consists of a system of  $SO_4$  ions in hexagonal close packing alternating with metallic ions. The K ions form a single hexagonal lattice, while the Li ions are arranged like the  $SO_4$  groups. The lattice dimensions by the powder method are those of a prism of base 5.13 A. U. and 8.60 A. U. high contg. 2 mols. of  $LiKSO_4$ . The space group is  $C_6^2$ . The  $SO_4$  ion is a tetrahedron of O atoms surrounding a central S atom, the sepn. S-O being 1.5-1.6 A. U.

S. C. L.

Geochemical distribution laws of the elements. IV. The crystal structure of the oxides of the rare earth metals. V. M. GOLDSCHMIDT, F. ULRICH AND T. BARYT. *Skrifter utgit av det norske Videnskap-Akademi i Oslo (I) Matem.-Naturvid. Klasse* 1925, No. 5, pp. 5-24; cf. *C. A.* 17, 3664; 18, 3160.—The sesquioxides of the rare-earth metals ( $R_2O_3$ ) have crystal structures belonging to three types, A, B and C. A is the high temp. form and C is the low-temp. form. A is hexagonal. B probably consists of two sub-groups,  $B_1$  and  $B_2$ .  $B_1$  is pseudo-trigonal.  $B_2$  has been observed only in the case of  $Gd_2O_3$ , and has higher symmetry than  $B_1$ . C is cubic, with a unit cube side of about 10 A. U., containing 16 mols. of  $R_2O_3$ . The space group is  $O_h^2$ . X-ray measurements were made by the powdered crystal method. On the basis of the structures of their oxides, the rare-earth metals may be divided into two groups. The cerite group contains La, Ce, Pr, Nd and Sm; and the ytterbite group contains Sm, Eu, Gd, Tb, Dy, Ho, Er, Tu, Yb and Lu. The cerite group forms oxides belonging to type A, while the ytterbite group sesquioxides belong to type C. The metals of both groups which are in the middle of the series also form oxides belonging to type B. The A and  $B_1$  modifications are enantiotropic. Whether  $B_2$  and C are enantiotropic is not decided.  $CeO_2$  and  $TbO_2$  have the fluorite structure with  $a = 5.40$  and  $5.57$  A. U., resp. Black praseodymium oxide, with a formula corresponding to  $Pr_2O_{11}$ , and brown terbium oxide, represented by  $Tb_2O_7$ , give strong diffraction patterns of the fluorite type, with weak lines corresponding to the C form of the sesquioxides. These two substances are either mixed crystals or double salts of the di- and sesquioxides. The length of side of the unit cube of the C form decreases with increasing at. no. in the rare-earth series. The cube sides for elementary cubes containing 16 mols. of  $R_2O_3$  are: Sc, 9.79; Y, 10.60; Sm, 10.85; Eu, 10.84; Gd, 10.79; Tb, 10.70; Dy, 10.63; Ho, 10.58; Er, 10.54; Tu, 10.52; Yb, 10.39; Lu, 10.37 A. U. There is a grouping into pairs according to chem. properties which is also shown in the lengths of cube sides. In general, the chem. properties of the rare earths and the lattice dimensions of the C form of their sesquioxides show a distinct correlation.

R. J. HAVIGHURST

The investigation of the properties of thin films by means of X-rays. W. H. BRAGG, *Proc. Roy. Inst. Gr. Brit.* Jan. 10, 1925, pp. 1-10.—A popular lecture, discussing lubrication, structure of soap films, surface tension, and catalysis in the light of X-ray studies on molecular orientation.

R. J. HAVIGHURST

Study of soaps and fats by means of X-rays. JEAN-JACQUES TRILLAT, *Compt. rend.* 180, 1838-40 (1925).—In connection with work on the mol. orientation of fatty acid in the form of films (cf. *C. A.* 19, 1072, 2150) a study was made of the influence of the supporting substance. The films were prepd. as before and examd. by the rotating-crystal method. Expts. with films of palmitic acid showed that whereas some metals furnish a spectrum identical with that obtained with a glass base, other metals furnish a second spectrum superposed on the first. This second spectrum is attributed to the

formation of a thin film of soap with a definite orientation surmounted by a thicker film of pure acid. Each furnishes its own spectrum, the relative intensities of which serve as a criterion of the affinity between the acid and the metal and the tendency to form a soap. It is suggested that the method may be of value in studying contact reactions. The soap spectra are particularly intense with Pb, Sn and Sb, less so with Fe, Cu and Bi, faint with Ni, Zn and Mo and absent with Al, Pd, Pt and Au. The spectra of all soaps of the same acid have a reticular distance of 46.3 Å U. (except Cu with 43.5 Å U). Moreover instead of an intensification in odd orders and a weakening in even order (cf. de Broglie and Trillat, *C. A.* 19, 2299), the intensity decreases uniformly, probably on account of the fact that only the metal atoms refract. Further expts. with various Pb soaps (from the stearate to the caproate) show that the change in the reticular distance is very uniform, viz., about 1.3 Å U. for each  $\text{CH}_2$  group, which is greater than that of the fatty acids but of the same order of magnitude as their esters. The greater part of the fats and waxes can be orientated by simple fusion on glass, giving a means of identifying them by their spectra. Thus the reticular distances of glyceryl margarate, hydrogenated soy-bean oil, spermaceti, Chinese wax, white ceresin and lecithin are 48, 47, 42.7, 42, 39.1 and 47 Å U., resp. Lecithin gives a particularly intense first order of reflection, which suggests its use in the spectrographic study of soft X-rays.

C. C. DAVIS

Some chemical deposits of a regular form. J. M. MULLALLY, *Phil. Mag.* 49, 1222-5 (1925).—A study of the thickness of the deposit of  $\text{NH}_4\text{Cl}$  in a glass tube in which  $\text{HCl}$  and  $\text{NH}_3$  (in air) are diffusing into one another from opposite ends. The thickness was measured by focusing a microscope through the wall on the inner crystals. Two curves meeting at the point of greatest thickness express the thickness ( $m$ ) as a function of the distance ( $l$ ) from that point in the two opposite directions.  $m/m_0 = e^{-kl}$  and  $m/m_0 = e^{-k'l'}$  where  $k$  and  $k'$  are consts. for a given tube,  $m_0$  is the max. thickness when  $l = 0$ ;  $k$  and  $k'$  remain const. as the deposit grows and unchanged with the diameter of the tube for narrow tubes (quill size). If  $L$  and  $L'$  are the distance from the sources of  $\text{NH}_3$  and  $\text{HCl}$ , resp., to the origo (point of max. deposit),  $kL$  and  $k'L'$  are const. in 3 different-sized tubes and have the values 575 mm. and -260 mm., resp.

S. C. LIND

Graphic treatment of the simple gas laws. BR. ECK AND E. KAYSER, *Z. Ver. deut. Ing.* 69, 871-5 (1925).—If the gas equation  $p\bar{v} = RT$  be expressed in logarithmic form,  $\log p + \log \bar{v} - \log T = \log R$ , these variables can be plotted on axes parallel to the sides of an equilateral triangle by employing certain mathematical devices. Similarly,  $p\bar{v}^n = C$  can be converted into the form  $\log p + n \log \bar{v} = \log C$ , and simplified to an equation of the general type  $Ax + By = C$ , the equation of a straight line in a coordinate system whose axes are at an angle of  $60^\circ$  to each other. Graphs are presented illustrating the principle, and numerous examples show how they may be used in solving many kinds of problems, such as those based on the  $p\bar{v}$  diagram, heat change during change of state, compressors, combustion engines, work accompanying change in density, steam turbines, etc.

W. C. EBAUGH

Corrections for gas volumes for altitudes 700 to 600 mm. HARRY GAUSS, *J. Metabolic Research* 4, 415-22 (1923).—A table of logs for correction of a gas vol. to standard conditions at intervals of 1 mm. between 600 and 700 mm., and of 0.5 from 15 to 32. The 4 variables in the single factor are: (1) correction for barometric pressure, (2) correction for room temp., (3) brass-scale expansion, (4) vapor tension. The table will be of value to technical industries in the Rocky Mountain region as well as to experimenters in metabolism.

T. B. GRAVE

An equation of state and thermodynamic diagram for air at low temperatures. ARTHUR SELIGMANN, *Z. tech. Physik* 6, 237-50 (1925).—A 2-page diagram, drawn to scale, for air, together with a description of the methods of calcn. and use, is included. The compn.-pressure diagram for  $\text{O}_2\text{-N}_2$  mixts. is given for the  $80^\circ$  abs. isotherm. The crit. data, sp. heats and general thermodynamic properties are reviewed and discussed.

J. H. PERRY

The orientation of molecules in the surfaces of liquids. WM. D. HARKINS, 2nd Colloid Symposium Monograph, 1925, pp. 141-73.—H. considers the development of the concept of interfacial orientation, and many of his expts. in connection therewith; also the wedge theory of emulsions, mol. orientation as exhibited by the relations between the energy of surface formation and that of vaporization, energy of thermal emission, adsorption and distribution of substances between regions, relation at surfaces and interfaces, adsorption at interfaces.

JEROME ALEXANDER

Monomolecular films between liquids: Butyric acid between water and hexane and acetic acid between water and benzene. WM. D. HARKINS AND H. M. McLAUGH-

LIV *J Am Chem Soc* 47, 1610-3(1925)—The no. of mols in a monomol film of  $C_3H_7COOH$  between  $H_2O$  and  $C_6H_{14}$  was the same as found by Harkins and King (cf. *C A* 13, 1553) for  $C_3H_7COOH$  between  $H_2O$  and  $C_6H_6$ . The upper liquid phase ( $C_6H_6$  or  $C_6H_{14}$ ) had no effect on the area per mol. in the closely packed film of  $C_3H_7COOH$ . On  $H_2O$ ,  $AcOH$  forms an expanded film with an area of 50 sq. A. U. ( $50 \times 10^{-18}$  sq. cm) per mol. with  $C_6H_6$  as the upper layer this area was reduced to 38.7 sq. A. U. Tables give the interfacial tensions of the system  $H_2O-C_6H_{14}$  with  $C_3H_7COOH$  as the solute and of  $H_2O-C_6H_6$  with  $AcOH$  as the solute. The ds. of both phases are given and the distribution of the solute is represented in each case by the values for the concn ratios  $C_W/C_B$  and  $C_W^1/C_B$  or  $C_W/C_N$  and  $C_W^2/C_N$ . H. M. McLAUGHLIN

Adsorption experiments with solutions. E. BEAL AND E. WACHENDORFF *Kolloid-Z. Special No.*, Apr. 1, 1925, 36-40.—The adsorption of the following substances by each of 6 different kinds of C and by  $SiO_2$  gel has been measured: (1) crystal violet dissolved in  $H_2O$  and in tetralin; (2) brucine dissolved in  $H_2O$  and in toluene; (3)  $I_2$  dissolved in KI and in toluene. The amt. of crystal violet adsorbed was measured colorimetrically. The brucine was measured by means of the Haber-Lowe interferometer in which a liquid chamber was inserted for measuring the concn. of the soln. (cf. *C A* 4, 3024). The different kinds of C adsorbed 5-18 times as much crystal violet from the soln. in  $H_2O$  as in the tetralin and approx. 4 times as much  $I_2$  from the soln. in KI as in the toluene. For brucine the different kinds of C varied, 3 adsorbing more and 3 adsorbing less from the soln. in  $H_2O$  than from the soln. in toluene. The no. of mg. of each substance adsorbed by 0.1 g. of  $SiO_2$ -gel. was: crystal violet in  $H_2O$  22, in tetralin 840, brucine in  $H_2O$  87, in toluene 123,  $I_2$  in KI 3, in toluene 0. The results show that the hydrophobic and hydrophilic character of the adsorbent is an important factor in adsorption and that in choosing a suitable adsorbent for removing a substance from a soln., the behavior of the adsorbent towards the solvent must be tested. The adsorption values were set in parallel with the heat of wetting of each adsorbent with  $H_2O$  and  $C_6H_6$ . The adsorbent which gave the smallest heat of wetting, in general, had the greatest capacity for removing the solute. H. M. McLAUGHLIN

The adsorption of water vapor and of some other vapors by a glass surface. D. HUART. *Compt. rend.* 180, 1594-6(1925)—A weighed quantity of  $H_2O$  was introduced into an evacuated vessel of known vol. and the resulting pressure at a const. temp. was measured on a Hg manometer. The difference between the calcd. and observed pressure was taken as a measure of the  $H_2O$  vapor adsorbed by the glass surface. The adsorption was practically proportional to the area of the glass surface and to the pressure of the vapor. Even at a vapor pressure as low as that obtained by evacuation in the presence of  $P_2O_5$ , there remained adsorbed about 0.009 mg.  $H_2O$  per  $cm^2$ .  $Alc$ , chloroform, benzene and toluene showed much less adsorption than  $H_2O$  vapor. The app. described can be used to det. the vapor d. of very volatile liquids with a precision surpassing that obtained by the Victor Meyer method. R. L. DONCH

Influence of the adsorbed substance on the adsorption capacity of adsorbents. Tests of adsorption capacity. TH. SABALITSCHKA AND W. ERDMANN. *Z. angew. Chem.* 38, 568-72(1925)—The importance of adsorption in the physiological action of certain medicines has only recently been appreciated. Several methods for testing the adsorptive power of medicines toward methylene blue solns., I solns., etc., have recently been employed to measure the efficacy of medicines whose physiological action is due to adsorption. However, numerous tests by the authors show that the relative order of adsorption by a series of medicinal adsorbents varied, depending on the substance adsorbed and the nature of the soln. in which the adsorption test was carried out. This specific influence of the adsorbent must be considered in comparing adsorption medicines, and of practicable the adsorption capacity of the medicines should be measured in a soln. contg. the substance whose removal by the medicine is desired. R. L. D.

A phenomenon of intense adsorption shown by tricalcium phosphate. PIERRE JOLIBOIS AND JACQUES MAZE-SENCIER. *Compt. rend.* 181, 36-7(1925).— $Ca_3(PO_4)_2$  pptd. by adding  $H_3PO_4$  to a large excess of  $Ca(OH)_2$  shows high adsorption for the latter, the ratio  $CaO/P_2O_5$  in the ppt. after 48 hrs. standing being 4.5 instead of 3, when 14 mols. were used. Even ignited  $Ca_3(PO_4)_2$  showed a marked adsorption for  $Ca(OH)_2$ . A. W. FRANCIS

Proof of the form of ultramicros. H. SIEDENTOPF. *Kolloid-Z. Special No.*, Apr. 1, 1925, 1-14.—An attempt to use the light entering a second medium by total reflection for observation of the scintillations from the faces of the unround ultramicros failed. Michelson's expts. on the measurement by the use of the interferometer of fixed stars which are too small for the ordinary telescope has been extended to the micro-

scope to develop a method of measuring ultramicros. Equations expressing the mathematical relations are developed. H. M. McLAUGHLIN

Dispersoids of the mineral world and of slags. R. LORENZ AND W. EITEL. *Kolloid-Z. Special No.*, Apr. 1, 1925, 41-4.—A general discussion of the colloidal phenomena, "pyrosols" (cf. *C. A.* 5, 3192). The solidified metallic fogs are considered as colloidal sols of solid disperse phases in solid dispersion mediums. They are typical representatives of a large no. of naturally occurring substances, especially the allochromatic minerals which are colored by finely divided pigments, e. g., pitchstone, ruby, sapphire, fluor spar, rock salt, the sulfide silicates from smelters, etc. H. M. McL.

Ultramicroscopy and coagulation. A. DE G. ROCASOLANO. *Kolloid-Z. Special No.*, Apr. 1, 1925, p. 80-2.—General discussion. H. M. McLAUGHLIN

Plasticity in colloid control. E. C. BINGHAM. *2nd Colloid Symposium Monograph* 1925, pp. 106-13.—B stresses the importance of plasticity along the lines brought out in his book "Fluidity and Plasticity." By using long capillary tubes and properly evaluating seepage and slippage, the formula  $V = \mu(F-f)r$  will probably be found to hold over a wide range of shearing stresses. Here  $\mu$  is the mobility (the reciprocal of the consistency  $\zeta$ ),  $F$  the shearing stress in dynes per sq. cm., and  $r$  the distance between the two shearing planes. "Notwithstanding that clear and indubitable evidence has now been found that in suspensions the flow is a linear function of the shearing stress, and the yield value obtained is quite independent of the dimensions of the instrument, nevertheless in colloids of the emulsoid type, evidence is found for exactly the opposite conclusions. The flow of emulsoids through a long capillary is not a linear function of the shearing stress, and the yield value cannot be obtained by simply extrapolating the flow-stress curve, for with capillaries of different radii non-concordant values for the yield value would be obtained." This evidence (to be published later) was obtained by Hood, Arnold and B. To explain the sharp distinction between the two types of colloids, it must be recalled that internal friction is due to two causes: (1) *diffusional viscosity*, resulting from interdiffusion of molecules having different amts. of transitional energy, (2) *collisional viscosity*, caused by actual spacial interference as the layers are sheared over each other. In liquids far removed from the crit. temp. (1) is of small importance, and the viscosity due to (2) follows Batschinski's law that fluidity is proportional to free vol. Chem. combination consequent on heat or pressure may qualify the law, which applies to suspensions as well. In suspensions a third cause of internal friction is the rotation of particles in the shearing process, energy being continually absorbed from the external stress in breaking down transient "structures." Hence flocculation increases yield value. Work is being continued on the structure effects in emulsoids. In many cases "m. p." is without scientific value. J. A.

Influence of very small quantities of foreign substances on the stability of colloidal solutions. A. BOUTARIC AND (Mme.) Y. MANIÈRE. *Compt. rend.* 180, 1841-2 (1925).—A table is given on the stabilization of  $As_2S_3$  sols. by the chlorides of Li, K,  $NH_4$ , Cd, Mg, Ba and Al and by  $Na_2SiO_3$ ,  $NH_3$  and KOH against flocculation by  $H_2SO_4$  and H, Li, K,  $NH_4$ , Cd, Mg, Ba and Al chlorides. J. T. STERN

Emulsions. WM. SEIFRIZ. *J. Phys. Chem.* 29, 834-41 (1925), cf. *C. A.* 19, 2433.—VI. Effect of acidity on type and reversibility of emulsions. Observations on the effect of acidity on the behavior of emulsions of olive oil precludes ascribing to acidity the prime role in detg. type or reversibility in emulsions. VII. Effect of phase ratio and of method in handling an emulsion type. Alteration of the phase-vol. ratio has no effect on the type of emulsion of petroleum oils of light weight stabilized by casein; but petroleum oils in or near the zone of instability are readily influenced by change in ratio of oil and  $H_2O$  phases. The observations cannot be accounted for by either of the two existing theories on the mechanism of emulsion type, viz., surface tension and orientation of mols. Methods in handling influence the emulsion type particularly with petroleum oils which lie in the zone of instability. VIII. A comparison of the behavior of vegetable oils with that of petroleum oils. Olive, sperm, castor-bean, poppy-seed and cod-liver oils, all form stable water-in-oil emulsions with casein as emulsifying agent. Linseed oil forms a dual emulsion, the water-in-oil type being the more stable. All are reversible by NaOH and after reversal may be brought back to the original type by  $BaCl_2$  or  $Ba(OH)_2$ . Vegetable oils are like the light petroleum oils as to type but differ from all petroleum oils in their behavior in the presence of electrolytes. HARRY B. WEISER

Sols with non-spherical particles. HERBERT FREUNDLICH. *2nd Colloid Symposium Monograph* 1925, pp. 46-56.— $V_2O_5$  sol shows the *Majorana phenomenon* (double refraction in a magnetic field) and streaks when stirred, due to *dityndallism*, which is conse.

quent on elongated shape of the particles—probably rod-like crystals. Other similar phenomena are discussed

Studies with the kinoultramicroscope. E. O. KRAEMER 2nd Colloid Symposium Monograph 1925, pp 57-69—Among the phenomena followed were: size and distribution of particles, e. g., in a Hg sol; verification of Einstein and Smoluchowski theories of probabilities and molecular statistics, gel structure (following the formation of a weak gelatin jelly containing some Hg sol), formation and coagulation of colloid particles. With gelatin, the viscosity appears to increase gradually, but in the later stages the motion appears to be localized more highly than would correspond to a simple viscosity effect. With some gels (e. g., Mg arsenate, dibenzoylcystine), increasing viscosity is not so evident, and gel formation occurs comparatively suddenly, following an "induction period," probably corresponding to development of an initial supersat. and condensation. With dibenzoylcystine gel, moving fibers were seen. On melting, gelatin gel shows preferential melting places. An alk. soln. of  $\text{Ba}$  tartrate was reduced by light, and a Carey Lea Ag sol was coagulated by light. Relatively large particles of the latter still showed active Brownian motion. In the initial stages, the aggregation of particles seems to be reversible spontaneously so that the union between particles in agglomerates must be loose and flexible.

New method for the determination of the distribution of size of particles in emulsions. A. J. STAMM 2nd Colloid Symposium Monograph 1925, pp 70-9—The principle of the method is similar to that of Wiegner (C. A. 14, 81) and of Ostwald and Habn (C. A. 16, 3773), but so modified and improved that emulsions with a rising dispersed phase may be studied, e. g., benzene in soap solns. The distribution curves showing particle sizes were obtained from the exptly. detd. accumulation curves by Svedberg's method, and duplicate detns. check fairly well. Changes in concn. alter the max. but slightly. K. oleate tends to give emulsions with larger drops than K. palmitate, in harmony with the wedge theory. Homogenization increased dispersity with soaps, but broke emulsions with gelatin or fatty acids as stabilizers.

Centrifuging, diffusion and sedimentation equilibrium of colloids of substances with high molecular weight. THE SVEDBERG, *Kolloid-Z.* Special No. 53-64 (Apr 1, 1925)—A brief description is given of the ultra-centrifuge (cf. C. A. 19, 596). The new diffusion app. consisted essentially of 2 columns of liquid—one the soln. to be studied and the other the solvent—joined at their lower ends through a 3-way cock so that the solvent column was the lower. Concn. curves were detd. by means of microphotometric measurements of the photographs taken of the columns from time to time. The diffusion const. was calcd. from these data. The app. and methods described can be used in many ways for measuring the size of particles and the detn. of the distribution of the size of particles and the mol. wt. of colloids highly dispersed and of compds. of high mol. wt. In certain cases the devices can be used for the study of hydration and electrolytic dissociation as well as for measuring the adsorption of electrolytes on particles. A theoretical discussion of the phenomena occurring is included.

The theory of swelling and reversibility phenomena in colloids. W. BILTZ *Kolloid-Z.* Special No. 49-52 (Apr 1, 1925)—The following equations based on the conception of lattice energy have been applied to the problems of swelling and reversibility. The heat of formation  $Q' = A' - E = A' - (U_0 - U_2)$ .  $E$  is the work done in bringing the ion or mol. from its position in the first to its position in the second lattice,  $U_0$  and  $U_2$  are the corresponding lattice energies and  $A'$  is the energy developed by the chem. combination with the central atom. For the case of strong hydration the following is approx. true:  $E \cong U_0[1 - 1/\{D^3/\pi[1 - (1/\pi)]\}]$  in which  $\pi$  is the exponent of Born's repulsion terms and  $D$  is the dilation, i. e., the quotient of the vol. of the hydrate and the vol. of the anhydride. Evidently swelling is possible only with a relatively small  $U_0$ . An ionic lattice with a large  $U_0$  due to electrostatic forces would be less capable of swelling than a mol. lattice. Substances with large swelling capacity (albumin, polysaccharides, lipoids and hides) have a mol. lattice and a relatively small  $U_0$ . When  $D$  is variable, a high mol. vol. would produce the same effect, e. g., soap. Thermal and mechanical data show that anhydrides like corundum and quartz have a large  $U_0$ . They show no swelling capacity. Unlimited swelling leads to reversible solns. of hydrophile colloids which are formed from substances with small  $U_0$ . Substances with large  $U_0$  form only metastable, irreversible colloidal solns., e. g., metals and insol. salts. When colloidal solns. are stabilized by protective colloids, the particles of the protective colloid are added to the submicrons of the irreversible colloid and oppose the lattice forces which tend to build up the larger crystals.

The influence of hydrogen-ion concentration on the protective action of gelatin

on Zsigmondy's standard gold sol. H. V. TARTAR AND J. R. LORAN. *J. Phys. Chem.* 29, 792-8 (1925).—A study of the influence of  $p_H$  on the protective action of gelatin on Au sol made by the HCHO method shows that between  $p_H$  values 8 and 5 the protective action remains constant. Below a  $p_H$  of approx. 4.7 the protective action decreases very rapidly with increase in H-ion concn. F. L. BROWNE

A new pattern formed by colored salts in solid gels. R. R. RIEGEL AND LEO WIDGOTT. *J. Phys. Chem.* 29, 872-4 (1925).—A 5% gelatin cake of rectangular cross-section and contg. 0.03%  $K_4Fe(CN)_6$  was submerged for 2 days in  $CuSO_4$  soln. On cutting a section of the cake a small portion at the center was free from  $Cu_2Fe(CN)_6$  ppt but contd.  $CuSO_4$ . Radiating from this clear center to the sharp edges were clear zones, the remainder being filled with  $Cu_2Fe(CN)_6$ . If the corners are rounded these zones extend only half way out from the central clear portion. With cakes having triangular cross section analogous clear zones were obtained. With gelatin gel contg. 0.1%  $K_2CrO_4$  in  $Pb(NO_3)_2$  soln. similar clear zones were found, but the portions contg.  $PbCrO_4$  ppt exhibited Liesegang rings. "The formation of well-marked clear zones reaching to the corners when the edges are sharp indicates that the entering sol. salt travels in straight lines perpendicular to the walls of the cake." F. L. BROWNE

The use of diffusion coefficients for the determination of the molecular weight of heavy amphoteric oxide hydrates in alkaline solution. G. JANDER AND H. SCHULZ. *Kolloid-Z. Special No.* (Apr. 1, 1925), pp. 109-18.—In order to avoid errors due to dissociation and hydration Reike's (cf. *Z. physik. Chem.* 6, 561 (1890)) equation  $D\sqrt{M} = k$ , has been changed to  $D_1\sqrt{M_1} = D_2\sqrt{M_2}$  in which  $D$  is the diffusion coeff. and  $M$  the mol. wt. The diffusion coeffs. of K tantalate and of another complex substance,  $Na_3(I(MoO_4)_4)$ , of known mol. wt. and as nearly as possible of the same structure were detd. by the method of Ohlms (Z. physik. Chem. 50, 312 (1904)) and the mol. wt. of K tantalate calcd. by substitution in the modified equation.  $D_1$  for the diffusion of K tantalate into  $H_2O$  was relatively high, 0.432, into 0.1 N KOH or 0.1 N  $KNO_3$ , 0.238 and into N KOH, 0.223. When  $D_1$  is 0.24,  $D_2$  0.29 the mol. wt. of K tantalate is 1750. Since the mol. wt. of  $Na_3(I(MoO_4)_4)$  taken as 1202 may be too high this result agrees reasonably well with the formula  $K_2(Ta(TaO_4)_4)$ . H. M. McLAUGHLIN

The solubility of carbon dioxide in water at low concentrations. KURT BUCHT. *Soc. Sci. Fennica Comm. Phys.-Math.* 2, No. 16, 1-9 (1925).—Ten expts. are reported on the soly. of  $CO_2$  in  $H_2O$ . The temps. varied from 17° to 20° and the absorption coeffs. from: 0.090 to 0.150. The results are: (where temp. is given first, followed by the absorption coeff.): 19.2-0.0930; 18.9-0.090; 19.1-0.0985; 18.2-0.098; 19.6-0.102; 17.2-0.095; 19.3-0.097; 19.5-0.110; 20.2-0.150; 18.7-0.156. J. H. PERRY

The solubility of sucrose. P. MONDAIN-MONVAL. *Compt. rend.* 181, 37-40 (1925).—The limiting heat of soln. of sucrose in  $H_2O$  was found by extrapolation of direct thermochem. measurements, -1.84 cal.; by combination of initial heat of soln. and heat of diln., -1.70 cal.; and by calcn. from soly. and van't Hoff's const. ( $i = 1.79$  from vapor pressure measurements), -1.77, agreeing within exptl. error, showing that the laws of soln. are obeyed. The soly. of sucrose in g. per 100 g.  $H_2O$  is as follows: 0.9°, 180.5; 15.8°, 196.0; 25.6°, 210.5; 30.5°, 218.0. The cryoscopic point is at -13.9° and 166 g. A. W. FRANCIS

The miscibility of mixtures of water, ethyl alcohol and isobutyl alcohol. PIERRE BRUN. *Compt. rend.* 180, 1745-7 (1925).—The soly. curve of  $H_2O$  and iso-BuOH was detd. by noting the temp. at which mixts. of known compn. became turbid. The critical temp. is 123.5° and the critical mixt. contains 37.5% of iso-BuOH. The triangular graph for the system  $H_2O$ -iso-BuOH-EtOH was similarly obtained from the soly. isotherms at 0°, 40°, 80° and 120°. At 0° the crit. mixt. contains 31.6% iso-BuOH, 15.7% EtOH, and 52.7%  $H_2O$ . ARTHUR GROLLMAN

Study of the displacement of some organic acids from their sodium salts by means of electrical conductivity. J. BUREAU. *Compt. rend.* 181, 42-4 (1925).—By electro-metric titration of solns. of salts of weak acids with HCl, the displacement of the acid was indicated by the error from the true titration. The residual combined org. acid varies from 0 for 0.1 N solns. to 0.075 for 0.00025 N (AcOH). Values for various mono- and dibasic acids and mixts. are given. A. W. FRANCIS

Ionization of two electrolytes in alcohol-water mixtures; influence of environment on ionization. F. BRADLEY AND W. C. M. LEWIS. *J. Phys. Chem.* 29, 782-91 (1925).—The ionizations of salicylic acid and cyanoacetic acid are detd. in all ratios of EtOH +  $H_2O$  at 25° and 35° by cond. measurements. By theoretical derivation all values are accounted for up to 48% EtOH. J. T. S.

The conductivity of solid salts at high temperatures. P. VAILLANT. *Compt.*

rend 179, 530-2 (1924); cf. *C. A.* 16, 2632.—When NaCl is placed between metal electrodes and a current is passed through then as the temp. is raised, the cond. passes through a max. and then a min. and then increases rapidly, becoming large when about 420° is reached. The latter increase follows an exponential law. On cooling and reheating the first max. is much lower, having indeed nearly disappeared. The remainder of the curve, however, approx. repeats itself. At low temps. the ratio  $i/I^{1/2}$  = current and  $I$  the voltage) is const. at low voltages but varies with voltage as the latter increases. For high temps.  $i/I$  is const. for all voltages measured. K<sub>2</sub>SO<sub>4</sub> and KCl are entirely analogous to NaCl. With BaCl<sub>2</sub> the results are a little more complicated. With increasing temp. two max. and two min. are obtained in the cond. On successive heating immediately following the first, only one max. and one min. are obtained. E. P. WIGHTMAN

Role of the superficial layer in the electrical conductivity of solid salts. P. VAILLANT. *J. phys. radium* 5, 81-91 (1924); *Sci. Abstracts* 27A, 914; cf. *C. A.* 16, 2632.—The effects of temp. on the elec. cond. of several solid salts has been studied somewhat more precisely than previously and the cond. has been found to be mostly superficial, as a result of an ionized layer of air, varying in degree with the amt. of moisture contained. E. P. WIGHTMAN

Studies on oxidation-reduction. VIII. Methylene blue. W. MANSFIELD CLARK, BARNETT COREN AND H. D. GUNES. *Pub. Health Repts.* 40, 1131-201 (1925); cf. *C. A.* 19, 2038.—Methylene blue is of very varying compn. and difficult to purify. The numerous samples which were studied show active impurities in the titration with benzoquinone, the same applying to Lauth's violet. Methylene white solns. are sensitive to light; its rate of oxidation by air varies as the fifth root of the OH-ion concn. A new set of buffer solns. using citrates is described, and oxidation-reduction potentials are measured at different  $p_H$ . Methylene blue must be regarded as a very strong base, while Lauth's violet has a basic dissociation const. of  $1.9 \times 10^{-14}$ . The reductant in each case fixes 1 H ion and 2 amino groups have basic dissociation consts. as follows: methylene white,  $K_1 = 1.4 \times 10^{-14}$ ,  $K_2 = 6.3 \times 10^{-16}$ ; leuco Lauth's violet,  $K_1 = 3.8 \times 10^{-14}$ ,  $K_2 = 4.3 \times 10^{-16}$ . The characteristic potentials at  $p_H = 0$  and 30° are 0.532 v. for methylene blue and 0.563 v. for Lauth's violet. The corresponding free energies of hydrogenation are calcd., and an equation is developed for the relation with the  $p_H$ . Bernthsen's constitutional formula and Wieland's theory of H transport are discussed. The Schardinger reaction on milk and the test for putrescibility of sewage are controlled electrometrically and various other applications of methylene blue are discussed. Methylene blue does not behave as a reliable reduction indicator. Extensive bibliography. J. T. S.

The influence of hydrogen ion on the mechanism of ferric salt reduction by sodium thiosulfate. JOSEF HOLLEY AND ALFRED MARTIN. *Z. anorg. allgem. Chem.* 144, 321-38 (1925); cf. *C. A.* 19, 789, 924.—By increasing HCl concn., the reduction of ferric salts by Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> is (1) retarded by a neutral salt action, (2) is retarded in weak acid soln. by a displacement of the equil.  $Fe^{+++} + 2HS_2O_4^{--} \rightleftharpoons Fe(S_2O_4)_2^{--} + 2H^+$  to the left with a consequent diminution in the concn. of the complex  $Fe(S_2O_4)_2^{--}$ , which is one of the reactants, and (3) is favored by suppressing the hydrolysis of the ferric salt. At higher acid concns. a 4th-order side reaction starts, in which ferric and thiosulfate ions are able to react directly, and at a concn. of 0.5 N, it prevails. For high acidities and slow reaction velocities, the reaction,  $S_2O_4^{--} + H^+ \rightleftharpoons HSO_4^- + S$  sets in and causes a decrease in the values of the 4th-order const. obtained. The temp. coeff. at 0.4 M was 2.93. D. S. VILLARS

Decomposition of hydrogen peroxide by cobaltic hydroxide. F. G. TRYBORN AND G. JESSOP. *J. Chem. Soc.* 127, 1320-30 (1925).—The decompn. of Merck's "perhydrol" (unstabilized) was followed at 25 ± 0.02° by detg. the rate of evolution of O<sub>2</sub> at const. pressure. The decompn. bulb was vigorously shaken by motor. Co(OH)<sub>3</sub> as catalyst for this decompn. showed an irreversible fall of activity, and a reversible increase varying inversely as the concn. of H<sub>2</sub>O<sub>2</sub>. By varying separately each factor in the reaction, it was found that (1) the apparent activity of a given mass of catalyst increases with addn. of traces of NH<sub>3</sub> to an approx. const. max.; (2) the initial activity of the catalyst is proportional to its amt.; (3) the catalyst activity is an inverse linear function of the H<sub>2</sub>O<sub>2</sub> concn. A mechanism is suggested in which the decompn. occurs in a monomol. film on the catalyst surface, a distortion of the intramol. field of force on adsorption rendering one H atom of the H<sub>2</sub>O<sub>2</sub> removable by the impact of an OH-ion. The HO<sub>2</sub> thus formed decomposes to give O and OH ion. An equation derived on this basis is shown to agree with exptl. data, and to be applicable to other cases of catalysis.

The stability of  $H_2O_2$  in vessels lined with paraffin wax is thus attributable to the non-polar nature of the surface. A. R. M.

The toxicity of thiophene for catalytic nickel and another action of catalytic copper. B. KUBOTA AND K. YOSHIKAWA. *Sci. Papers Inst. Phys. Chem. Res. (Japan)* 3, 33-50 (1925).—The decrease in activity of catalytic Ni for the hydrogenation of benzene, containing 1% of thiophene, was studied at 800°. Though rapidly poisoned as a result of the formation of NiS, it maintains its activity for the hydrogenation of phorone giving undiminished yields of valerone. Reduced Cu is not affected by thiophene as regards its ability to hydrogenate either  $C_6H_6$  or phorone. The  $m.p.$  of the semicarbazone of valerone is found to be 121° instead of the lower values recorded in the literature. The rapidity with which Ni is poisoned depends for the most part on the temp. at which it was reduced, reduction at higher temps. facilitating the poisoning action. Other factors involved in its prepn. have but a slight effect. ARTHUR GROLLMAN

Platinum-resistance thermometry at low temperatures. M. S. VAN DUSEN. *J. Am. Chem. Soc.* 47, 326-32 (1925).—The usual Callendar formula for resistance thermometers fails below -40°. Henning and Heuse have proposed a low-temp. formula which requires 3 calibration points, -0°, Hg  $m.p.$ ,  $O_2 b.p.$ . The Hg  $m.p.$  can be calcd. quite well enough from the ordinary calibration. A more convenient equation is then obtained by adding to the ordinary Callendar equation a term,  $\beta(1/100 - 1)^2/100^3$ , which is detd. by the  $O_2 b.p.$ , and is only needed below -40°. The same equation can be obtained with a slight loss in precision, by substituting the Hg  $m.p.$  for the  $S b.p.$  in the calibration. This equation agrees with that of H. and H. to about 0.01° at -120°, which is as good as the observations. W. P. WHITE

The heats of solution and of decomposition of chlorine dioxide. HENRY BOOTH AND E. J. BOWEN. *J. Chem. Soc.* 127, 342-5 (1925).—The heat of soln. is 6600  $\pm$  200 cal. per mol. from a "large no. of detns.," and is independent of the concn. of the soln. The heat of decompn. was observed by starting the decompn. with an elec. spark in a Dewar flask which was calibrated by a small amt. of elec. energy. The extreme discrepancy was about 11, the result, 23,500 cal. per mol. By combination with the heat of dissociation of  $Cl_2$ , 55,000 cal., the heat of decompn. to  $Cl + O_2$  is 4000 cal. This result leads to a theoretical discussion. Gaseous  $ClO_2$  has a band spectrum of groups of lines with approx. const. frequency difference, which according to modern theory is to be "attributed to changes of vibrational quanta superimposed upon an electronic activation quantum change." From the observed const. frequency difference,  $2 \times 10^{13}$ , by the relation  $Q = Nh\nu$ ,  $Q = 2000$  cal. for one vibrational quantum. But vibrational quanta begin to appear among the mols. not far above the ordinary temp. Thus only 2 vibrational quanta are needed to give a  $ClO_2$  mol. enough energy for decompn. Since the gas is nevertheless remarkably stable thermally "it would appear that energy of vibration is not sufficient to activate a mol. chemically, but that electronic activation is required." W. P. WHITE

The  $C_p T$  or  $C_p O$  diagrams and the true (instantaneous) specific heat. WITOLD JAZDYNA. *Z. tech. Physik* 6, 261-2 (1925).—A discussion of methods of obtaining the true sp. heats from  $C_p T$  diagrams. A diagram of  $C_p$  vs. the degree of superheat for water vapor is included. J. H. PERRY

Remarks on the dissipation of heat of reaction. M. BORN AND J. FRANCK. *Ann. Physik* 76, 225-30 (1925).—Theoretical. The uniting of 2 atoms to form a mol. liberates an amt. of heat equal to the heat of dissociation; hence, since the atoms previously had some energy, it has been supposed that the mol. must break up again unless some energy is immediately liberated. This has been supposed to occur either through a third atom, which is involved in the act of union and escapes with some of the energy, or through radiation. Mols., however, frequently have more energy than corresponds to the heat of dissociation, e. g.,  $H_2$ , absorbing light between 800 and 1200 A. U., receives 3 to 5 times the energy of dissociation, and is saved from breaking up by the excitation of the many-line spectrum. Energy of ionization and rotation can bring the total above the heat of dissociation. Nevertheless, in all cases there is a loss of energy. In the union of neutral atoms this cannot be by radiation, but must be by a 3rd atom. Even in the formation of polar NaCl the immediately resulting radiation would be of a kind that has not been observed in numerous attempts. The radiation observed in such cases is of a kind that involves a 3rd atom. Radiation can occur on the union of an electron or ion with a neutral atom or mol. The relative frequency of such radiation or of the 3rd atom action is a function of the pressure. W. P. WHITE

The determination of energy and absolute temperature by means of reversible processes. C. CARATHÉODORY. *Sitzb. preuss. Akad. Wiss.* 1925, 39-47.—Rather abstract method of dealing with the fundamentals of thermodynamics. W. P. W.

Sodium by electrolysis through glass. R. C. BURT. *J. Optical Soc. Am.* 11, 87-91(1925).—Na ions were made to pass electrolytically through evacuated glass elec. light bulbs. The bulb was dipped in molten  $\text{NaNO}_3$ . The filament was lighted until it began to emit electrons. A positive terminal of Cu wire was immersed in the salt bath. The emitted electrons were carried to the glass wall opposite the molten salt by the field. These electrons neutralized Na ions in the glass, which thus became atoms. These were evapd. by the heat at the bottom of the bulb and condensed as metallic Na at the top. Na ions from the molten salt replaced those of the glass and migrated through it, being in turn neutralized at the inner surface. By proper wiring to prevent overheating and ionization between the filament leads it was possible to deposit nearly 300 mg. of Na per hr. with a 60 w., 110 v. lamp. The electrolysis followed Faraday's law at least to 1 part in 500. Neither K ions nor Li ions could be passed through glass by this method. By heating the bulb to a sufficiently high temp. a brilliant Na arc suitable for resonance radiation studies was produced. The Na produced is spectroscopically extremely pure, K not being present in amts. greater than 1 part in 500,000. The app. is useful for lecture table expts. R. L. DODGE

The hydrogen-electrode function of platinum. K. HOROVITZ, *Sitzb. Akad. Wiss. Wien* 132, 367-73(1924), *Science Abstracts* 28A, 255.—A Pt wire, by an alteration of the H-ion concn. of the soln., experiences an alteration of e. m. f. in the same sense as a H electrode, but the value of the e. m. f. of the acid alkali chain is smaller.

H. G.

The decrease in electromotive force of unsaturated Weston cells. WARREN C. VOSBURGH. *J. Optical Soc. Am.* 11, 59-62(1925).—Further measurements were made of the e. m. f. of a large no. of unsatd. Weston cells after standing for a year or more in the dark at room temp. (cf. *C. A.* 18, 615, 2995). The e. m. f. was found to decrease at the av. rate of 0.03 to 0.04 mv. or 0.003 to 0.004% a year. The decrease for individual cells in which the electrolyte contained between 0.03 and 0.05 mols. of  $\text{H}_2\text{SO}_4$  per l. varied between 0.01 mv. and 0.07 mv. a year. A properly made unsatd. cell is a satisfactory working standard of e. m. f. where results accurate to not more than 0.01% are desired. An unsatd. cell should be checked against a more const. standard at least once in 2 years.

R. L. DODGE

The application of the quinhydrone electrode to the measurement of  $p_{\text{H}}$  value in solutions containing copper ions and other bivalent ions. JASPER B. O'SULLIVAN. *Trans. Faraday Soc.* (advanced proof) (July 6, 1925); cf. *C. A.* 15, 2074; 16, 1607.—The potential of the cell  $\text{H}_2$ -acid + electrolyte—same acid + electrolyte + quinhydrone—Pt varied from -0.7038 to -0.7043 where the acid was 0.005 N sulfuric and the salt 0.05 N Na, Mg, Zn, Ni, Co, Fe or Cd sulfate. The potential of a cell made up of neutral 0.1 N  $\text{CuSO}_4$  can be satisfactorily measured and gives an upper limit of 0.072% to the degree of hydrolysis of the  $\text{CuSO}_4$ .

D. S. VILLARS

Specific electrokinetic changes between solid phases of different chemical composition and electrolytes of the solution in contact with them. RICHARD LANGE. *Z. physik. Chem.* 116, 1-64(1925).—Electrokinetic processes are those which obtain when two phases in contact take on opposite charges. A mathematical analysis of the double layer gives for the electrokinetic potential (the p. d. between the inside of the solid phase and the boundary between freely movable liquid and the immovable film on the solid particle)  $\zeta = \epsilon(1/\epsilon\beta h)$  where  $\beta = 10^8 \pi \sqrt{\epsilon}$ ;  $n$  = valence;  $\epsilon$  = concn. of the ion;  $h$  = thickness of the film on the particle; and  $\epsilon$  = the Nernst potential (the potential between the inside of the solid phase and the inside of the soln.);  $\zeta$  has the same sign as, and varies in magnitude roughly with,  $\epsilon$ , and the factors which affect the magnitude and sign of  $\epsilon$  should have a similar effect on  $\zeta$ . Electrolytes which introduce an ion which has a small soly. product with the cation were used and the electrokinetic potential was measured by the amt. of electroendosmosis.  $\zeta$  exptl. corresponded fully with  $\epsilon$  calcd. from soly. product relations for the ppts.  $\text{BaSO}_4$ ,  $\text{PbCrO}_4$ ,  $\text{Zn}_2\text{C}_2\text{O}_4$ , and  $\text{AgCl}$ .

D. S. VILLARS

Study of salt compounds in the electric arc. T. PECZALSKI AND G. MOKRZYCKI. *Compt. rend.* 180, 1829-31(1925).—The potential of an arc shows a characteristic drop, related to the m. p. or b. p. of a salt in the electrode crater. Studies are made with  $\text{Al}_2\text{O}_3$  +  $\text{CaO}$  which show compd. formation and  $\text{KCl}$  +  $\text{NaCl}$ .  $3\text{KCl}$  +  $\text{NaCl}$  is indicated at the arc temp. as the effective compd.

J. T. STERN

Electrical charges arising at a liquid-gas interface. H. W. GILBERT AND P. E. SRAW. *Proc. Phys. Soc. (London)* 37, 195-214(1925).—This is a comprehensive review with bibliography of the work done on the p. ds. and elec. charges which arise at the liquid-gas interface, under the following headings: p. d. at the interface at rest; cataphoresis of gas bubbles; passage of gas over a liquid without rupture of the latter; fall of liquid

in an unbroken column through a gas; jets; waterfall electricity; and electrification produced by bubbling gases through liquids, shattering drops in an air stream, and spraying a liquid. D. S. VILLARS

The thermodynamics and kinetics of liquid chains. H. SCHILLER *Sitzb. Akad. Wiss., Wien* 132, 11a, 353-65 (1924); *Science Abstracts* 28B, 114.—Electrode potentials and diffusion potentials, i. e., potentials between points in electrolytes near the electrode, influence one another. The latter potentials should be eliminated in calcg. electrode potentials, but the expts. of Fales and Vosburgh (*C. A.* 12, 2062) throw doubt on the validity of Planck's formula in the case of HCl, KCl and HgCl. The thermodynamic methods of Helmholtz, Nernst, Planck and P. Henderson for the calcn. of diffusion potentials involve the mobility of the ions, a quantity which should not enter into thermodynamic (equil.) equations. This was pointed out by H. A. Lorentz in 1916, who considered, moreover, that the methods of statistical mechanics could not cover the whole domain of thermodynamics. Debye then gave a kinetic theory of concn. cells, substituting mol. Brownian movements for the osmotic pressure, but retaining the representation of the elec. field by a potential. S. exams. the method and theories mentioned, and also the papers of Debye and Huckel (*C. A.* 17, 2665; 18, 100) and concludes that neither the thermodynamic nor the kinetic theories can be considered satisfactory. A thermodynamic method is in general inadmissible; the kinetic hypothesis of Debye involves assumptions which are not of kinetic character; a complete kinetic theory has not yet been given. S. does not accept Lorentz's view, however, that the methods of statistical mechanics and of thermodynamics could not entirely coincide. H. G.

Magnetization of ferro-nickel (saturation and atomic moment). MARCEL PEACHARD. *Compt. rend.* 180, 1836-8 (1925).—Curves are given for the satn. values of the intensity of magnetization of 30 Fe-Ni mixts., ranging from 0 to 100% Ni, at +16, -79 and -188°. From these, by extrapolation, the curve for -273° is obtained. These curves indicate the formation of the compd. Fe<sub>3</sub>Ni. A curve is also given for the at. magnetic moment of the Fe-Ni series. This curve is flat from the % corresponding to Fe<sub>3</sub>Ni to that corresponding to FeNi<sub>2</sub>. The at. magnetic moment for this part is 9 Weiss magnetons. W. W. STIFLER

Magneto-chemical researches on the formation of fixed chains and of nuclear groups in organic compounds. PAUL PASCAL. *Compt. rend.* 180, 1506-7 (1925).—Values of the mol. magnetic susceptibility are given for 23 org. compds. and these values are correlated with the structure of the resp. atoms. W. W. STIFLER

Various magnetic states of an ion. G. FOEX. *Compt. rend.* 180, 919-21 (1925).—Specimens of the same salt often possess varying magnetic properties which appear to be connected with distinct structural differences in the paramagnetic ion which they contain. This diversity, which has already been examd. for salts in aq. soln. (*Ann. phys.* 16, 174 (1921)), is now extended to cryst. salts. A specimen of ferrous NH<sub>4</sub> sulfate has been prepd., corresponding with 26 magnetons and possessing a strong positive mol. field, there being in addn. a sudden change in the direction of the temp. coeff. of magnetization curve at 100°. A specimen of the same salt examd. by Jackson (*C. A.* 18, 1947) corresponded with 27.5 magnetons, the mol. field being very weak and the influence of temp. quite normal. Anhyd. Co sulfate has been shown to exist in 2 forms, the varieties having 25 and 24 magnetons, resp., the resp. magnetic fields being negative and feebly positive. B. C. A.

Investigation of the refractive index of zinc selenide and zinc telluride. J. A. WASASTJERNA. *Soc. Sci. Fennica Commentationes Phys.-Math.* 2, No. 7, 1-10 (1925).—For ZnSe  $n = 2.89$ ; for ZnTe  $n = 3.56$ . J. H. PERRY

Refraction and dispersion of gaseous benzene. J. A. WASASTJERNA. *Soc. Sci. Fennica Comm. Commentationes Phys.-Math.* 2, No. 13, 1-9 (1925).—The effect of a change of d on mol. refraction is reported. A new method for detg. the refraction and dispersion in the gaseous phase, of substances which are liquid under atm. pressure, is described. The refractive index of gaseous benzene, reduced to standard temp. and pressure indicated by  $\nu$  is given by  $(\nu-1) = (P_0/P)(\nu_0-1)$ , in which  $\nu_0$  is the refractive index of dry, CO<sub>2</sub>-free air at 0° and 760 mm. The dispersion was detd. by white light; reduced to standard temp. and pressure, it is indicated by  $\theta = \nu_F - \nu_C$ . Taking  $\nu_0 = 1.0002922$  and  $\theta_0 = 0.0000029$ , there is calcd. from the exptl. data:  $\nu_D = 1.001821$  and  $\theta = 0.0000454$ . J. H. PERRY

The influence of solvents upon rotatory power. RENE LUCAS. *Compt. rend.* 181, 45-7 (1925).—The ratio  $\delta'/\Delta = ([\alpha]_A - [\alpha]_B)/([\alpha]_A - [\alpha]_C)$  for a compd. in 3 solvents, A, B and C, which is independent of wave length, holds also if B is a mixt. of A and C, probably because the compd. may exist in 2 distinct forms each with definite rotatory power. The relative proportion of the 2 forms varies with the solvent, temp., concn.

etc. Alkylcamphors, dialkylcamphors, fenchol, fenchone, isoborneol, and camphor have been studied. A. W. FRANCIS

Preliminary experiments on feather pigments. W. D. BANCROFT. *J. Phys. Chem.* 28, 1147-50 (1924).—Some red and yellow feather colors are very resistant to extn with alc, while others are not. The reds and yellows which are not easily extd by alc are fast to light and *vice versa*. The red and yellow pigments give yellow solns in alc, which are apparently identical. It is not known whether the red pigment is converted into the yellow at the time of extn, or differs structurally from the yellow pigment. The extd pigment acts like an acid dye. It does not dye cotton directly and dyes wool most strongly in an acid bath and least in an alk. bath. It is taken up to some extent in alumina. The feathers were obtained from a no. of species of birds.

CHAS. H. RICHARDSON

Heat and atomic motion (MORESSÉE) 9. The strength of materials as a resultant of atomic forces (MORESSÉE) 9. The relation of the electric conductivity of an element to its position in the periodic table (ERSTERY) 3.

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### 3—SUBATOMIC PHENOMENA AND RADIOCHEMISTRY

S. C. LIND

The direct measurement of the mean free path of uncharged silver atoms in nitrogen. FRIZ BIELOZ. *Z. Physik* 32, 81-102 (1925).—The values for the scattering of a ray of uncharged atoms by collision with gas molecules is calculated and confirmed exptly. within a 10% exptl. error by absorption measurements made with an Abbe microspectroscope according to Wien's method. Between the pressure limits 1 and  $7 \times 10^{-3}$  mm. Hg the product of the gas pressure and the mean free path is a const. The radius of the Ag atom is calculated to be 1.0 A. U.

F. O. ANDEREGG

Problems of atomic physics. B. CABRERA. *Scientia* 37, 307-18 (1925).—The electrostatic theory and Bohr's model, the Bohr-Sommerfeld law of the emission spectra and their weak points are discussed. The significance of the dielectric const., the phenomena of radioactivity and the disintegration of the atom by  $\alpha$  rays is pointed out. Chem. reactions seem to affect the superficial electron shells only. The profound changes, however, caused by certain chem. reactions are strongly suggestive of the participation of the inner shells or even the nucleus in the reaction. One of the properties intimately related to the structure of the atom is diamagnetism, a fact not sufficiently realized by the chemists. Bohr's magneton failed to receive exptl. confirmation. Interesting exptl. data have been accumulated in connection with Weiss' magneton theory, which was advanced some time before Bohr and is based on the exptl. fact that the magnetic moments of all atoms have a common divisor, which is called Weiss' magneton. There is

an satisfactory explanation for its origin. Weiss' law seems to indicate a certain discontinuity in the arrangement of the intra atomic orbits, since any magnetic field is due to the movement of elec. charges. The Weiss magnetism, about  $1/2$  of the Bohr magneton, was found sometimes to change suddenly without a seemingly adequate chem. change. The frequent occurrence of fractional magneton nos. would necessitate the assumption that most metals are mixts. of several kinds. MARY JACOBSON.

**Static model for helium.** H. S. ALLEN. *Proc. Roy. Soc. Edinburgh* 44, 116-28 (1924).—By assuming the existence of a quantum force as postulated by Langmuir (*C. A.* 16, 3383), acting along the line joining 2 charged particles, such models have been deduced for the neutral He atom, the neutral He atom, and the He mol. The introduction of 3 quantum nos. renders the models admissible by the choice of these nos. The results obtained for the atom are in agreement with the original model of Bohr, but are not in agreement with the experimentally det'd ionization potential. For the mol., the moment of inertia obtained is of the same order of magnitude as that det'd by Curtis from the band spectrum. H. C. A.

**Duration of the quantic state  $2p_1$  of the mercury atom.** P. RANKETI, *Atti and Lincei* [vi], 1, 223-5 (1925).—In view of the discordant values published for the mean duration of the Hg atom in the  $2p_1$  state, the monochromatized light from a Hg lamp, immersed in cold water, was passed through the slit of a revolving disk into Hg vapor contained in a quartz flask. Photographic examn. revealed no trace of resonance in the Hg vapor even when the interval between excitation and observation was reduced to  $5 \times 10^{-8}$  sec. Conclusion: The  $2p_1$  condition is not metastable at the ordinary temp. At  $200^\circ$ , the resonance condition begins to exhibit sensible duration, but the phenomenon is then complicated by the appearance of a green fluorescence, attributable to a mol. Hg, formed by the shock between an excited and a normal atom and possessed of a long life. The spectrum of the green fluorescence observed when Hg is shaken in an evacuated vessel at about  $200^\circ$  shows, besides a continuous band resulting from the yellow to the violet, also the more intense of the Hg lines, such as 5780, 5780, 5780, 5780 A. U., and, less strongly, 2536 A. U. This excitation is evidently analogous to recombination by friction. H. C. A.

**The quantum conditions.** G. WATAHIN. *Z. Physik* 32, 650-62 (1925).—Mathematical. H. C. U.

**Formal foundations of the new mechanics.** K. SCHAPARSKINIKOW AND W. S. FUDOKOV. *Z. Physik* 32, 661-72 (1925).—An attempt is made to devise a general mechanic method which will apply to both electrons and light quanta. H. C. U.

**The quantum theory of paramagnetism.** I. TAMM. *Z. Physik* 32, 682-95 (1925).—The Pauli Sommerfeld theory of paramagnetism is expanded by introducing other values of the Landé splitting factor than 2. When the Sommerfeld normal for the inner quantum numbers is used, the Weiss magneton nos. can be calcd. for the ions  $Ti^{+++}$ ,  $V^{+++}$ ,  $Cr^{+++}$ ,  $Mn^{+++}$ ,  $Cr^{++}$ ,  $Mn^{++}$ ,  $Mu^{++}$  by assuming that the normal states are  $s_{1/2}^2$ ,  $s_{1/2}^2$ ,  $s_{3/2}^2$ ,  $s_{3/2}^2$ ,  $s_{1/2}^2$ ,  $s_{1/2}^2$ ,  $s_{3/2}^2$ , resp. In the symbol  $s_{j/2}^2$ ,  $s$  is the multiplicity of the term,  $j$  is the inner quantum no. and  $s$  is the usual designation of the  $s$  terms. For the above ions  $r$  increases by integers beginning with 1 and  $j$  by halves beginning with 0 as the no. of valence electrons remaining or the ion increases by integers beginning with 0. The magneton number of  $V^{++}$  agrees with that calcd. for a  $s_{1/2}^2$  state. Difficulties are met in the case of the ions  $Fe^{+++}$ ,  $Fe^{++}$ ,  $Co^{++}$  and  $Ni^{++}$  and these are discussed in detail. The normal states of  $Fe^{++}$  and  $Co^{++}$  are probably partially inverted  $d_{3/2}^1$  and  $d_{5/2}^1$ , resp. The magneton no. calcd. for  $Co^{+++}$  agrees well with the exp't. value. The possible effects of hydrolysis of the ions are discussed. H. C. U.

**The magnetic  $\beta$ -ray spectra of radium E.** IRVING CURIE AND JEAN D'ARLÈVE. *Compt. rend.* 181, 31-3 (1925).—A narrow beam of  $\beta$  rays, deflected by a linear source and narrow Pb slit parallel to the source, falls on a photographic plate several cm. from the slit and is divided and dispersed into a spectrum by a magnetic field of 100 to 400 gauss-cm. The principal band of  $\beta$  rays of Ra E is sharply bounded on the side of large velocities at  $\beta = 0.936$  and terminates indefinitely on the small velocity side toward  $\beta = 0.70$ . A broad max. between  $\beta = 0.88$  and  $\beta = 0.80$  is interpreted as two bands overlapping, one covering the range  $\beta = 0.936$  to  $\beta = 0.80$  and the other extending from  $\beta = 0.88$  to  $\beta = 0.70$ . A feeble  $\beta$  radiation of velocity greater than that of the principal band exists for  $\beta = 0.986$  to  $\beta = 0.97$ . The energy in volts corresponding to  $\beta = 0.936$  is 2,600,000 v. W. P. MUMFORD.

**Experiments on crystal structure by means of radioactive substances.** K. HARA. *1172. Sitzb. Akad. Wiss. Wien* 132, 114, 375-85 (1925); *Science Abstracts* 28A, 161,—In

connection with the more recent work on the growth of crystals and adsorption, the necessity is recognized of following what takes place in the new-formed limiting layer. The possibility of doing this offers itself in the use of radioactive gases to give active deposits which are known to be in monomol layers. Expts. are described on the adsorption of Th B and C at a crystal surface, which appear to make it probable that, in the main, only those atoms are adsorbed of which combination with the electronegative constituent part of the lattice is fugitive. Expts. on polished pieces of zinc blend with surfaces parallel to the positive and negative tetrahedra show that the adsorption is dependent on the different orientations of the crystal surfaces. H. G.

Radioactivity of the Guérat granite. P. LOISEL. *Compt rend* 179, 533-4(1924); *Science Abstracts* 28A, 130.—Detns on the Rn obtained from the granite of Guérat, Bagnols-de-l'Orne, indicates the presence of substances of long life which have not yet been isolated (cf. C. A. 17, 491). H. G.

Electric currents across spaces. H. ROHMANN. *Z. Physik* 31, 311-25(1925).—For metallic electrodes sepd. by small distances and relatively low voltages in a high vacuum, the extinction voltage, so long as the electrode sepn is const., is const. and independent of the current strength within wide limits. It is proportional to the distance between the electrodes. Below the extinction voltage no current passes, and by observing its value, the crit. field strength can be easily detd. The latter is independent of the electrode material although it drops appreciably on long evacuation. F. O. ANDEREGG

Quasineutral electric diffusion in stationary and flowing gas. W. SCHOTTKY AND J. V. ISSENDORFF. *Z. Physik* 31, 163-201(1925).—Vapor from a Hg discharge tube distd. into a side tube provided with a negative electrode seems to give a positive ion current with satn characteristics. When the side tube is heated the current falls to a negligible value. If the electrode is positive somewhat larger currents will pass. A theory is developed where the behavior is quasineutral ( $\pi^+ - \pi^-$ ) for the three cases of positive and negative unipolar and ambipolar diffusion, considered in the light of field and space charges and with reference to the detn. of the density distribution,  $n$ . The differential equations and limiting conditions are the same for  $n$  in all 3 cases, but not when diffusion occurs because of different diffusion consts. The most important special cases are treated, such as stationary gas or gas flowing in the same direction in which it diffuses. This theory, applied both to the wall current in large rectifiers and to the expts. described in this article, gives for both the unipolar and ambipolar diffusion const. in Hg vapor a magnitude of 3000 cm<sup>2</sup>/sec. F. O. ANDEREGG

Theory of the stratified discharge. A. GÜNTHER SCHULZE. *Z. Physik* 31, 1-13 (1925).—After a careful analysis of the stratified discharge it is concluded that the known laws for the motion of electrons in gases in the glow discharge are sufficient to explain all of the striations by assuming increasing and intensifying space charges developed by the alternately varying velocity of the electrons. It is not necessary to assume any new method of ionization. F. O. A.

The peculiarities of radiation cells of great electric resistance. E. BODIN. *Compt. rend.* 180, 1731-3(1925).—Cells made of various feebly conducting salts and oxides emit short-wave radiations when an elec. current traverses them (cf. C. A. 18, 2340). For a given potential at the electrodes, the current diminishes with the time and most of the potential drop inside the cell occurs at the electrodes. The limiting intensity radiated is not proportional to the p. d. at the electrodes. These results were obtained on radiating cells of HgO, HgSO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, CuSO<sub>4</sub>, BaSO<sub>4</sub>, CuCO<sub>3</sub>, etc. D. S. VILLARS

A new method of producing slow cathode rays. G. REBOUL. *Compt rend* 180, 1735-7(1925).—A radiation cell (cf. C. A. 18, 2340; *Compt. rend.* 180, 916) of high elec. resistance projects + and - charges according to the potential on it. It was shown that the negative charges are cathode rays of velocities ranging from 50 to 450 v. by two different methods, one utilizing resonance potentials and the other, antagonistic fields. The potential drop at the electrodes, as detd. by Bodin (cf. preceding abstract) is of this order and must therefore cause the emission of these electrons. D. S. VILLARS

Theoretical considerations on the direction of photoelectron emission. PIERRE AUGER AND FRANCIS PERKIN. *Compt. rend* 180, 1742-4(1925).—The probability of photoelectron emission from the solid angle  $d\Omega$ , is derived to be  $\sin^2\alpha d - \sin^2\lambda d\lambda$ , for a beam travelling along the X axis and polarized with its elec. vector parallel to the Z axis, where the solid angle  $d\Omega$  is in the direction  $OV$ , whose azimuth is  $\lambda$  and angle with the X axis is  $\alpha$ . D. S. VILLARS

Experimental study of directions of photoelectron emission. PIERRE AUGER. *Compt rend* 180, 1939-41(1925).—A. compares the number of  $\beta$  rays emitted in a gas

within the angle  $\omega$  (measured from the direction of the X-ray) with the integral,  $\int \sin^2 \omega d\omega$ , and the number emitted within the azimuthal angle with the integral,  $\int \sin^2 \lambda d\lambda$ . The agreement is satisfactory. These integrals are taken from A.'s formula for the probability of photoelectron emission in a solid angle  $d\omega d\lambda$ ,  $p = \sin^2 \omega d\omega \sin^2 \lambda d\lambda$  (cf. preceding abstract).

D. S. VILLARS

Modification of laws of emission of ions from hot metals by the quantum theory. S. C. ROY. *Proc Indian Assoc Cultivation of Science* 9, 61-81(1924). *Science Abstracts* 28A, 142-3.—Although the classical electron theories of metals, developed by Drude, Lorentz, Thomson and others, have given a fair account of the various outstanding phys. properties of metals, such as the heat and elec. cond., the Peltier effect, the Thomson-effect, the Richardson-effect and so on, the various secondary hypotheses which have been been advanced to explain these phenomena are seldom convincing and are often in contradiction with one another. The most obvious difficulty, however, is the question of the heat capacity of metals. If the "free" conduction electrons could claim their full share in the equal distribution of kinetic energy, then this share of energy should be plainly noticeable in the at. heats of these bodies. Such an increase in the at. heats of metals as compared to metalloids which contain vanishingly few free electrons, has never been discovered. Further, as Lorentz has pointed out, the classical electron theory invariably leads to Rayleigh's law of radiation. In recent years the ideas have been developing that the law of equipartition of energy for the metallic electrons must be abandoned in favor of Planck's quantum law. The difficulty, however, lies in properly quantizing the motions of the metallic electrons and in explaining the thermal cond. of metals and the correctness of Wiedemann-Franz's law on such a quantized theory. Lindemann has pointed out that the expression "free" electron, suggesting or intending to suggest an electron normally not under the action of any force is really a contradiction of terms. It is, therefore, conceivable that metallic electrons, instead of forming an ideal gas, really constitute a condensed solid. In continuation of the conceptions of Born and Karman, it may be assumed that a metal crystal is constituted of interlocked space lattices of electrons, atoms or at. residues. Lindemann has drawn up a theory of metallic state on the basis of these ideas. J. J. Thomson has, recently, developed similar ideas in his electron theory of solids. The object of the present paper is to consider statistically the laws of emission of ions or electrons from hot metals on the basis of the supposition that the metallic ions or electrons behave in all manner like Planck's line vibrators while the emitted ones constitute an ideal monatomic gas. Conclusion: It would be premature to pronounce any definite opinion on the question of identity between photoelec. and thermionic work function, specially in view of the uncertainties in the detns. of the long wave-length limits. The data given here point to a general correspondence between the 2, and also make it abundantly clear that the work-function  $\phi$ —is a function of the at. vol. (See also C. A. 18, 1610) H. G.

Electrical conductivity and Hall effect for nickel films. A. RIEDE. *Z. Physik* 28, 177-215(1924).—Ni films have been prepd. by cathodic spluttering in H. Their cond. is proportional to their cross section even for the thinnest films. The Hall effect in such films is proportional to the field strength in weak magnetic fields, but approaches a limiting value in intense fields. The sign of the effect is negative. B. C. A.

The intensity of the Zeeman components. HELMUT HÖNL. *Z. Physik* 31, 340-54 (1925).—From the conclusions of Sommerfeld and Heisenberg drawn from Bohr's correspondence principle for the Zeeman effect a "correspondence rule" is developed with arithmetical intensification, which includes all the old rules and provides a general scheme for the intensity of all Zeeman components. F. O. ANDEREGG

Intensities of the components in the Zeeman effect. L. S. ORNSTEIN, H. C. BURGER AND W. C. VAN GEEL. *Z. Physik* 32, 631-3(1925); cf. preceding abstract.—The intensities of the components of the 4810, 4722 and 4680 triplet of Zn have been measured and found to agree with the rules derived from the study of other lines. H. C. U.

Intensities of components in the Zeeman effect. L. S. ORNSTEIN AND H. C. BURGER. *Z. Physik* 28, 135-41(1924).—A theoretical paper, giving a generalization of the rules already described (cf. C. A. 18, 3004) for the calcn. of the intensities of multiplets, which make it possible to predict the intensities of the components in the Zeeman effect. A preliminary announcement is made of exptl. verifications of the theory. B. C. A.

The relation of the electric conductivity of an element to its position in the periodic table of the elements. Z. A. ERSTEIN. *Z. Physik* 32, 620-38(1925).—E. shows that the function  $C_r V^{1/4}$ , where  $\epsilon$  is the sp. elec. cond. of polycrystalline elements at comparable temps.  $r$  and  $V$  is the at. vol.,  $C$  is a const., is a max. at the first element of each horizontal

series of the periodic table and that it decreases in a monotonic manner as we go from left to right across the table. By comparable temps. is meant temps. which are the same fraction for each substance of its boiling temp under atm. pressure. The calcs. were made at  $1/2$  of the normal b. ps. This function measures the "interatomic" cond. Its relative values for Na, Mg, Al, and for K, Ca, proportional to  $(8-n)^2$ , where  $n$  is the no. of valence electrons. For Cu, Zn and for Ag, Cd, In the function is proportional to  $(8-n)^3$  and for Au, Hg, Tl, to  $(8-n)^4$ . The agreement between the exptl. data and these rules is within about 5% and the accuracy of the data is such that the function cannot be calcd. more closely than this. The relations therefore may not be exact. It is suggested that the exponents 2, 3 and 4 are related to the sub groups in the electron shells of the atom. The work of others is discussed. H. C. U.

The momentum imparted to electrons by radiation. E. O. HULBERT and G. BREIT. *Phys. Rev.* 25, 193-6(1925).—Assuming (a) the theorems of conservation of momentum and energy and (b) the agreement of the light quantum theory with the wave theory in their estimates of the radiant energy scattered in various directions from a beam of electromagnetic radiation by a group of electrons, it is shown that the total momentum transferred to the electrons is the same on both theories and that  $\Delta V/V$  (where  $V$  is the velocity of the electron) is too small to detect exptly. even under very favorable circumstances. D. C. BARDWELL

Absorption coefficient for slow electrons in gases. R. B. BRODE. *Phys. Rev.* 25, 636-44(1925).—Electrons from a heated filament were accelerated through a slit and deflected magnetically around a circular path into a Faraday cylinder connected with a galvanometer. Absorption coeffs. were detd. for various accelerating voltages from 2 to 360 v. for A, He, CH<sub>4</sub>, N<sub>2</sub>, CO and H<sub>2</sub>. D. C. BARDWELL

Electron emission from oxide coated filaments. L. R. KOLLEA. *Phys. Rev.* 25, 671-6(1925).—Oxygen ( $10^{-4}$  mm.) decreases the electron emission of oxide coatings of BaO and SrO on Pt-Ir filaments. Argon, H<sub>2</sub>, CO and CO<sub>2</sub> increase it. Positive-ion bombardment increases it, while flashing at 1600° K. deactivates the filament. The distribution of velocities is Maxwellian, but the av. energy is nearly 30% higher than corresponds to the temp. of the filament. D. C. BARDWELL

The motion of electrons between coaxial cylinders under the influence of current along the axis. A. W. HULL. *Phys. Rev.* 25, 645-70(1925).—A study is made of the current from a large electrically heated filament to a coaxial cylindrical anode, limited by the circular magnetic field, as regards (1) the motion of the electrons, (2) plate current as a function of the voltage, (3) plate current as a function of the filament current. D. C. BARDWELL

The relative mobility of initial positive ions in gas mixtures at low pressures. H. B. WILKIN. *Phys. Rev.* 25, 630-5(1925).—The relative mobilities of the initial positive ions in gas mixts. at pressures of 30 to 60 mm. were detd. by the Franck-Rutherford alternating-potential method and ions produced by  $\alpha$ -particles of Po. In mixts. of C<sub>2</sub>H<sub>6</sub>Cl and H<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub>, and N<sub>2</sub> and C<sub>2</sub>H<sub>6</sub>Cl, two types of ions were found, indicating that aged ions are clusters. D. C. BARDWELL

The absorption coefficient for slow electrons in gases. R. B. BRODE. *Phys. Rev.* 25, 636-44(1925).—Measurement of the absorption coeff. of electrons of known velocity in A, He, CH<sub>4</sub>, N<sub>2</sub> and CO, showed max. values at certain voltages, in accord with the results of Mayer and Ramsauer (*C. A.* 15, 3933), for A and He. If showed no max. D. C. BARDWELL

Quantum theory of the intensity of the modified band in the Compton effect. G. E. M. JAUNCEY. *Phys. Rev.* 25, 723-36(1925); cf. *C. A.* 19, 1655.—The theory of the previous paper is extended to the scattering by L and M electrons and by electrons in elliptical orbits. For certain positions of the electron in each orbit the mass of the whole at. is added to that of the electron and the quantum is scattered without change of wave length. D. C. BARDWELL

Note on the dependence of the intensity of the Compton effect upon the atomic number. BERGEN DAVIS. *Phys. Rev.* 25, 737-9(1925). D. C. BARDWELL

The effect of magnetic fields upon the polarization of resonance radiation. P. RASSETTI. *Atti accad. Lincei* 33, n. 38-41(1924); *Science Abstracts* 28A, 116-7.—Wood and Ellett have recently described (*C. A.* 18, 1610) some interesting observations on the effect of magnetic fields upon the polarization of resonance radiation. They found that the resonance radiation normally observed with primary rays is usually polarized in a measure more or less strong. A magnetic field may destroy or augment the polarization according to its direction and to the condition of polarization of the primary ray. The intensity of field necessary to produce such effects is less than 1 gauss for Hg and about 100 gauss for Na. The object of the present paper is to describe some expts. carried

out upon Hg-vapor under different conditions from those employed by Wood and Ellett, and to show how all the observed facts may be repeated in a very simple manner and may be intimately connected with the Zeeman effect and with the orientation of the atoms in the magnetic field.

H. G.

The scattering of X-rays. P. DEBYE *J. Math. Phys.* 4, 133-47 (1925).—D. presents a first approximation theory to explain the interferences between different mols. in a liquid which yield the principal X-ray diffraction ring even for monatomic gases in the liquid state. Even if the mols. are comparable with hard spheres and do not interact in any other way than to prevent each other from entering into the domain defined by this sphere, this fact alone is sufficient to cause a scattering function exhibiting a max. at an angle defined by the quotient of the wave length and the diam. of the sphere. Thus by complex mathematical analysis, D. derives the equation  $I_m = N(\psi^2/R^2)(1 - (\Omega/V)\phi(2ksa))$  where  $I_m$  is the intensity max.,  $N$  = no. of particles of scattering gas,  $\psi$  = scattering factor defining amplitude and phase,  $R$  = radius vector of a point with axis of coordinates,  $\Omega = N(4\pi/3)(2a)^3$ , the total vol. of all spheres of action of all mols., each sphere having a radius equal to the diam. of 1 mol.  $a$ ,  $V$  = vol. occupied,  $\phi$  = function  $2ksa = 8(\pi a/\lambda)\sin(\phi/2)$ . In general a mol. will not act as a single resonator but will produce scattering also depending upon the at. frame. Hence there may be 2 kinds of interference effects, the "inner" and "outer." Since the "outer" effect is proportional to  $\Omega/V$ , by making measurements on a gas under different pressures it should be possible to eliminate the "outer" effect which tends to vanish with decreasing  $d$ , and hence by the "inner" effect to obtain direct measurement of the distance between 2 atoms in a mol. The generalized formula is  $I_m = 4N(\psi^2/R^2)(1/2)\{(1 + (\sin ksl/ksl))\}$  where  $ksl = 4\pi(l/\lambda)\sin(\phi/2)$  and  $l$  is distance from the scattering particles. Assuming  $2a/\lambda = 3$  and  $l = a$ , corresponding for  $\lambda = 0.7 \times 10^{-8}$  cm. to a diam. of the sphere substituting the mol. of  $2.1 \times 10^{-8}$  cm. and a distance of resonators substituting the atoms of  $1.05 \times 10^{-8}$  cm., D. plots 4 curves for  $\Omega/V = 0, 1/4, 1/2$  and  $1$ . The diagram shows how the first max., occurring at  $\theta = 12^\circ$  and corresponding to intermol. interference, disappears with decreasing  $d$  leaving a second max. at  $\theta = 45^\circ$  undisturbed, because this max. corresponds to the interat. interference of the 2 atoms in the mol.

G. L. CLARK

The mechanism of X-ray scattering. ARTHUR H. COMPTON. *Proc. Nat. Acad. Sci.* 11, 303-8 (1925); cf. *C. A.* 19, 1816.—On any spreading wave theory of radiation, including that of Bohr, Kramers and Slater, there should be no correlation between the direction of ejection of a recoil electron and that of the effect of a scattered quantum of energy, after a collision has taken place. On the quantum view, however, if the recoil electron is ejected at angle  $\theta$  with the incident X-ray beam, the scattered quantum should appear at an angle  $\phi$  such that  $\tan^2 \phi = -\cot \theta / (1 + \alpha)$ , where  $\alpha = h/mc\lambda$ . Two methods were used in an exptl. attempt to detect a correlation between the two angles. A two point counter, with chambers set at the proper angles, should catch simultaneous impulses. Cloud expansion photographs should show an occasional  $\beta$ -ray track produced by a scattered X-ray quantum correlated with the track of the recoil electron. Preliminary results by both methods uphold the quantum theory. That is, scattered X-rays proceed in directed quanta.

R. J. HAVIGHURST

Heavy-metal salts as fluorescent materials. A. GYEMANT. *Chem.-Ztg.* 49, 493-4 (1925).—Detailed directions are given for prepg. fluorescent  $\text{CaWO}_4$  and  $\text{Zn}_2\text{SiO}_4$  salts that are of great importance in X-ray work.

HARRY B. WEISER

Characteristic X-rays from lithium. G. K. ROLLEFSON. *Phys. Rev.* 25, 740-6 (1925); cf. *C. A.* 18, 1086.—The photoelec. method previously described was used to det. radiation and ionization potentials of Li. Radiation potentials were found at 39.2, 43.07 and 46.0 v., and the ionization potential at 48.4 v. The radiation potential at 43.07 v. corresponds to the  $K_\alpha$  line of Li, and this value is used to extend the Moseley curve for  $K_\alpha$  lines. The following values were obtained by interpolation; Li 283.5, Be 132.8, B 74.4, C 49.0, N 33.2, O 24.4, F 18.6, Ne 14.8 A. U.

D. C. BARDWELL

An investigation of the tungsten X-ray emission and absorption spectrum with a vacuum spectrometer. R. V. ZUMSTEIN. *Phys. Rev.* 25, 747-52 (1925).—With a cast bronze X-ray tube, a vacuum spectrometer, and a new type window of lamplack and collodion, the M series of W was studied both in emission and absorption.

D. C. BARDWELL

The separation of cerium and the arc spectrum of this element. J. BARDET and C. TOUSSAINT. *Compt. rend.* 180, 1936-8 (1925).—A method of rapidly increasing the hafnium (cerium) concn in Zr-Hf mixts. is based upon the difference in soly. of the phosphates in  $\text{H}_2\text{SO}_4$ . Seven series of pptns. gave a product contg. about 90% of Hf from an initial of only 2 to 3%. The arc spectra of the richest products were examd.

in the interval 2300 to 3500 Å. U. No lines were found which could be attributed to any other element but Hf or Zr. For the former all the lines given for Hf by Hansen and Werner (cf. *C. A.* 18, 627) were found and also a certain number of new lines. A table of 48 wave lengths (2324.45 Å. U. to 3421.5 Å. U.) is given. W. F. MEGGERS

Quantitative study of ultra-violet absorption spectra of dichloroethylenes. J. ERRERA AND VICTOR HENRI. *Compt. rend.* 180, 2049-50 (1925).—Mol. refracting power and dielec. const. having been shown to be different for the *trans* and *cis* derivs., the method of quant. absorption of ultra-violet rays is employed to study these two isomers in hexane and alc. solns. as well as in the pure state. For either deriv. absorption begins near wave length 2000 Å. U. and increases rapidly for shorter wave lengths, but *trans* always absorbs more than *cis*, the ratio of the absorption coeffs. being 1.3 at 2595 Å. U. and 3.9 for 2200 Å. U. This difference in absorption is the same for hexane solns. from  $1/10,000$  to  $1/1$ , for alc. solns., and for the pure liquids, indicating that the mols. are in the same state in the different solvents in spite of their difference in dielec. const. W. F. MEGGERS

Series in the absorption spectrum of water vapor. HOLGER WITT. *Z. Physik* 28, 249-55 (1924).—Since the  $H_2O$  mol. has 3 atoms one would expect to find in the absorption spectrum of water vapor three series corresponding to the three principal moments of inertia. A discussion of the available data for wave lengths from  $0.7 \mu$  to  $170 \mu$  leads to a tabulation of various bands, each being characterized by a const. wave-number difference between its lines. Three recurring differences of about 17, 24 and  $57 \text{ cm}^{-1}$  are believed to distinguish the 3 series above referred to. W. F. MEGGERS

Variation of the wave length of absorption lines of iodine with vapor density. A. PEROT AND M. COLLINET. *Compt. rend.* 180, 2030-2 (1925).—The pressure-effect on wave lengths of spectral lines has been frequently investigated but it appeared of interest to take up a particularly simple case, that of absorption by I vapor, to see if the wave length depends on the density. In order that the intensities of the absorption lines remain the same, comparisons were made of lines given by two tubes, contg. the same quantity of I, having the same diams. but different lengths. The variation of wave length was measured by an interferential method somewhat different from that used heretofore. The light from a 25-amp. arc passed through the absorption tube either 10 or 80 cm. long, both tubes being heated to  $180^\circ$  by the same elec. heater, and then filed a plane grating spectroscope and a concave mirror of 3.5-m. focus. An objective was placed so that its focal plane coincided with the spectrum, the light traversed an interferometer of 25 mm. thickness and was received by a telescope adjusted for infinity. Measurements on an interference system corresponding to a given radiation were made alternately with first one tube and then the other in the path. The interference rings enlarge on passing from the high density to a low density. By putting  $\delta\lambda/\lambda = a\rho$ , where  $\rho$  is the density in abs. value, it was found that  $n$  is independent of  $\lambda$  and of  $\rho$ , at least within the limits of the investigation ( $\rho = 0.16 \times 10^{-4}$  to  $1.96 \times 10^{-4}$ ); the order of magnitude of  $\delta\lambda/\lambda$  for these limits was  $2 \times 10^{-4}$ , and  $a = +12 \times 10^{-4}$ . For the lines studied (6034, 5993, 5956 Å., 5573, 5503, 5498 Å. U.) the wave lengths increased with the vapor density. From other expts. at atm. pressure it appears that only the density of I vapor is effective and not the total pressure. W. F. MEGGERS

The distribution of probabilities of transitions in the alkali atoms. HANS BARTELS. *Z. Physik* 32, 415-38 (1925).—Calculs. similar to those of W. Thomas (*C. A.* 18, 3533), but introducing some new mathematical approximation methods, are given. From the results of these calculs. the dependence of the av. life of the atom in the excited state upon the quantum no. is a direct consequence. G. L. CLARK

Tables and graphs for facilitating the computation of spectral energy distribution by Planck's formula. M. KATIERKINE FAENAFER AND C. L. SNOW. *Bur. Standards, Miscellaneous Publ. No. 56*, 7 sheets (5 charts) (1925). E. H.

Paschen-Back effect. C. RUNGE. *Ann. Physik* 76, 266-72 (1925).—A theoretical paper in which it is shown that Sommerfeld's interpretation (*C. A.* 16, 3032) of Voigt's theory of the Paschen-Back effect for the pairs of lines  $s-p_1$  and  $s-p_2$  is not in agreement with the facts, as is shown by Kent's work (*C. A.* 9, 551) on the splitting up of the Li line 6708 by a magnetic field. Kent's observation of the behavior of component 7, however, cannot be reconciled with R.'s views on the term resolution of spectral lines. B. C. A.

Absorption of electrically luminescent potassium vapor. A. L. NARAYAN AND G. SUBRAHMANYAM. *Proc. Indian Assoc. Cultivation of Science* 9, 15-8 (1924); *Science Abstracts* 28A, 124.—In order that a vapor may absorb light corresponding to a given series in its spectrum there must be a large no. of atoms with orbits corresponding to the first term of the pulse to be absorbed. The Bergmann series is therefore absorbed at

high temps., when the sharp series is emitted. This can be tested by keeping the vapor feebly luminescent instead of by raising to high temp. A glazed porcelain tube 50 cm. long wound with a heating coil was used. It was provided with Pt electrodes and plane glass windows kept cool by water jackets. To avoid disturbance of the Paschen galvanometer used with a mirror spectrometer, the tube was placed 30 ft. from the instrument and a beam of sunlight focussed through it. With the tube at  $350^{\circ}$  and no discharge, the first members of the diffuse and sharp series of K at  $1.18 \mu$  and  $1.25 \mu$  were observed, and also the first 2 members of the Bergmann series at  $1.52 \mu$  and  $1.1 \mu$ . When the discharge was passed, lines at  $0.58 \mu$  and  $0.53 \mu$  belonging to the diffuse and sharp series were also emitted and there was no appreciable absorption of the lines at  $1.25 \mu$  and  $1.17 \mu$ . There was a distinct absorption of the first Bergmann member at  $1.5 \mu$ , the galvanometer deflection being reduced from 12.4 cm. to 11.3 cm. H. G.

Rotatory powers of fluoro derivatives of benzene and its homologs as a function of the wave length. F. RIZZI. *Atti r. accad. Lincei* [vi], 1, 124-6(1925).—The curves representing the dependence of the optical rotation of fluorobenzene, fluorotoluene, fluoro-*m*-x., and fluoro-*m*-*o*-xylenes on the wave length exhibit a change in direction at approx. zero rotation, the rotation being dextro for red and levo for violet light. B. C. A.

Spectroscopic shift law. I. E. FUES. *Ann Physik* 76, 299-316(1925).—Theoretical. The relationship between the spectra due to similarly constructed atoms or ions, e. g., neutral Li,  $\text{Be}^+$ ,  $\text{B}^{++}$  and  $\text{C}^{+++}$ , or neutral Na,  $\text{Mg}^+$ ,  $\text{Al}^{++}$  and  $\text{Si}^{+++}$ , is discussed. B. C. A.

Intensity of multiple lines. E. FERMI. *Atti r. accad. Lincei* [vi], 1, 120-4(1945).—A theoretical interpretation is suggested for the empirical rules governing the intensities of the components of multiple lines. B. C. A.

Negative nitrogen band spectrum. M. FASSBENDER. *Z. Physik* 30, 73-92 (1924).—An extensive examn. of the negative N band spectrum has been made, precautions being taken to reduce to a min. intensity the bands of the second positive N group, which overlaps it in the violet and ultra-violet. Seven of the 20 bands observed have been measured and arranged in series. P and R branches, zero lines and intensity distribution have been detd. B. C. A.

Spectrometric methods of investigation of the infra-red. H. WIRT. *Z. Physik* 28, 236-48(1924).—The construction of sensitive bolometers and thermopiles for infra-red spectrometry is given in detail. In the course of testing the app. measurements of the infra-red absorption of water vapor were obtained. B. C. A.

The harmonic analysis of electron orbits. F. C. HOYT. *Phys. Rev.* 25, 174-86 (1925).—Harmonic analysis of the penetrating electron orbits in the Bohr atom assuming that the outer segments of the orbits are Keplerian ellipses and that the penetrating parts, which are traversed only a short time compared to the period of Keplerian motion, are continuation of the exterior motion, leads to coeff. agreeing fairly well with the values obtained by Thomas from spectroscopic data by the method of Fues. D. C. BARDWELL

The series spectra of two-valence-electron atoms of phosphorus ( $\text{P}_{IV}$ ), sulfur ( $\text{S}_{IV}$ ) and chlorine ( $\text{Cl}_{VI}$ ). I. S. BOWEN AND R. A. MILLIKAN. *Phys. Rev.* 25, 591-9(1925), cf. C. A. 18, 3537.—The study of the regular and irregular X-ray doublet laws for stripped atoms is extended to the spectra of two-electron atoms, where triplets and singlets occur instead of doublets. D. C. BARDWELL

The series spectra of three-valence-electron atoms of phosphorus ( $\text{P}_{III}$ ), sulfur ( $\text{S}_{IV}$ ) and chlorine ( $\text{Cl}_{V}$ ). R. A. MILLIKAN AND I. S. BOWEN. *Phys. Rev.* 25, 600-5 (1925); cf. preceding abstract.—An extension to three-electron atoms. Screening consts. of 1, 2 and 3 valence electron systems are collected in a table for Na to Cl. D. C. B.

Absorption and emission spectra of the Geissler discharge in mercury vapor and in mixtures of mercury and hydrogen. L. A. TURNER AND K. T. COMPTON. *Phys. Rev.* 25, 606-12(1925).—Absorption spectra of the positive column, continuous and striated, are photographed and the lines obtained discussed. Emission spectra of various parts of the discharge are photographed. D. C. BARDWELL

Absorption of a line of the principal series of singly ionized atomic mercury. L. A. TURNER AND K. T. COMPTON. *Phys. Rev.* 25, 613-7(1925).—Evidence is presented that the 1942 line is a member of the principal series and that the 2225 and 2848 lines are of the subordinate series of Hg. D. C. BARDWELL

Experimental determination of the relative transition probabilities in the sodium atom. G. R. HARRISON. *Phys. Rev.* 25, 768-82(1925).—Direct measurement of line absorption intensities was made for the lines 2 to 16 in the principal series of Na, by a precise method of photographic photometry. D. C. BARDWELL

Methods for determining transition probabilities from line absorption. J. C. SLATER *Phys Rev* 25, 783-90(1925) —The various steps in computation of quantum transition probabilities from measurement of absorption spectral lines are discussed. Cf preceding abstract

D. C. BARDWELL

Theory of the relation of spectral lines to mass variations within the atom. L. B. HAM *Phys Rev* 25, 762-7(1925) —Mathematical

D. C. BARDWELL

The intensities of lines in multiplets. I. Theory. H. N. RUSSELL. *Proc. Nat. Acad. Sci* 11, 314-22(1925) —Complex groups of related spectral lines known as multiplets are of 3 principal types —ordinary, rhomboid and symm. Recent work has shown that the intensities of the lines in a multiplet follow certain qual rules. The lines themselves arise from the change in energy content of the atom between two stages or levels which in turn are specified by certain quantum nos. Quant. expressions for the intensities of the lines of the 3 types of multiplets are worked out in terms of the quantum nos. on the basis of the sum-rule, which states that the sum of the intensities of the lines which have a given initial or final level in common is proportional to the statistical weight of this level. For large values of  $K$  and  $R$  (modified forms of the azimuthal and inner quantum nos.) an almost complete soln. is afforded by the correspondence principle.

C. C. KIESS

New light on two-electron jumps. R. A. MILLIKAN AND I. S. BOWEN *Proc. Nat. Acad. Sci* 11, 329-34(1925) —Atoms which have lost all but one of their valence electrons constitute one valence-electron systems and are defined as stripped atoms. When one and two electrons are permitted to return to stripped atoms they then become two-valence-electron systems and three valence-electron systems, resp. Hot-spark vacuum spectroscopy of such radiating systems has shown distinguishing groups of lines in the spectra of similar systems. In the two-valence electron systems these consist of 6 nearly equally spaced lines, and in the three-valence-electron systems of 4 closely grouped lines. These 4- and 5 line groups follow the irregular doublet law, i. e., they exhibit a linear progression of frequency with atomic no. The electron transitions occur between levels of the same total quantum no. These transitions involve the simultaneous jumping of two electrons, the sum of the changes in energy of both being the observed frequencies of the characteristic lines.

C. C. KIESS

Series spectra of two-valence-electron systems and of three-valence-electron systems. I. S. BOWEN AND R. A. MILLIKAN *Nature* 115, 422-3(1925) —The three laws characteristic of X-ray spectra, viz., (1) The Moseley law, (2) the regular-doublet law of Sommerfeld, (3) the irregular-doublet law of Hertz, have been shown to hold for optical spectra emitted by atoms of the same electronic structure but of varying nuclear charge. Results similar to those already found for the one-valence-electron systems Na I to Cl VII, have now been found for the two-valence-electron systems Mg I, Al II, Si III, P IV, S V, Cl VI, and the three-valence-electron systems Al I, Si II, P III, S IV, Cl V. Tables of terms calculated for the different spectra are given.

C. C. K.

The spark spectrum of chlorine. LÉONE AND EUGÈNE BLOCH. *Compt. rend.* 180, 1740-2(1925) —When fused NaCl is excited in an electrodeless tube by an oscillating discharge the salt is decomposed as the pressure within the tube is decreased, thus furnishing sufficient Cl gas to maintain the discharge. The spectra of Cl excited in this manner may be classified as arising from different degrees of excitation. Thus the lines 4819, 4810, 4794, and all those behaving similarly to them are classed as members of the first-order spark spectrum, Cl II. Lines which appear under conditions which bring out 3991, 3720, 3658, etc., are classed as members of the second-order spark spectrum, Cl III. Lines belonging to the arc spectrum Cl I, are not excited in this manner.

C. C. KIESS

Complementary investigations on the structure and distribution of band spectra. H. DESLANDRES *Compt. rend* 180, 1980-6(1925). —The relation previously found (*C. A.* 19, 2299) for expressing the members of band series in terms of a fundamental frequency  $d_1 = 1062.5$ , is shown to hold for the absorption bands of  $H_2O$  vapor. Two bands of which the fine structures have been measured (at  $3.15 \mu$  and  $6.26 \mu$ ) are represented by the formulas  $\nu = 18d_1/6 \pm \lambda d_1/24$  and  $\nu = 9d_1/6 \pm \lambda d_1/48$ , the one being twice the other. The significance of  $d_1$  as a common property of all atoms is discussed.

C. C. KIESS

The origin of the auroral green line 5577 Å. U. and other spectra associated with the aurora borealis. J. C. McLENNAN AND G. M. SIKKIM. *Proc. Roy. Soc.* 108A, 591-12(1925) —Uncondensed discharge through a tube contg He at 2-4 cm pressure and O at a partial pressure of 1 to 3 mm., developed the auroral green line at 5577.35 Å. U. With a mixt. of He and N the line was not obtained. With He, N and O, however, the line appeared together with the band spectrum of  $N_2$ , thus reproducing

in the lab. practically the entire auroral spectrum. With Ne and O the behavior of the green line was the same as with He. It is suggested that the upper atm. (above 110 km) contains 20 parts of He to one of O. High-speed electrons from the sun could ionize, or at least excite, the He atoms so that there would be a certain no. of them in a metastable state. The energy of such atoms colliding with a N mol. would be sufficient to excite the band spectrum of N. On collision with an O mol. the energy of the metastable He would not only dissociate the mol. but excite the atoms with consequent emission of the green line. C. C. KIESS

New investigations of spark spectra in the Schumann region. LÉON AND EUGÈNE BLOCH. *J. phys. radium* 6, 105-20(1925), cf. *C. A.* 19, 779, 934.—Vacuum spectrographs equipped with fluorite prisms and lenses were used to study the spark spectra of various elements in the region between 1850 Å U and 1300 Å U. With the improved app. the spectrograms exhibit a wealth of detail not attained hitherto in vacuum spectroscopy. The plates have been measured and the results derived from them are based on standards chosen from C and N measurements of Simeon, or of Hopfield and Leifson. In the tables detailed lists of lines are given for Fe, Ni, Co and W. C. C. KIESS

A spectroscopic study of the combustion of phosphorous trioxide and of hydrogen phosphide. H. J. EMELEUS. *J. Chem. Soc.* 127, 1362-8(1925).—The ultra-violet band spectra of the light from glowing  $P_2O_3$ , from pure  $PH_3$ , burning spontaneously in air under reduced pressure, and from the pure phosphide burning in  $O_2$  are identical with the spectrum of glowing P and that of the element burning normally. A variation in the relative intensity of the bands with the conditions has been noted. Certain substances which inhibit the glow of P and of  $P_2O_3$  can prevent the ignition of a  $PH_3$ -air mixt. when the pressure is reduced. The low temp. combustions of  $P_2O_3$  and  $PH_3$  involve some common stage responsible for the chem. anomalies and intimately bound with the characteristic light emission. A modification of Thorpe and Tutton's method of prepg.  $P_2O_3$  (*J. Chem. Soc. (London)* 57, 545(1890)) in which the P is burned under reduced pressure is described. G. L. CLARK

Determination of thorium X (GAZZONI) 7. A system of chemical elements and isotopes (SHCHUKAREV) 2.

BORN, MAX. Struktur der materie in einzeldarstellungen (Part II). Vorlesungen über Atommechanik (in 2 vols.) Vol. I. Edited by Friedrich Hund. Berlin: Julius Springer. 358 pp. G. M. 15. Reviewed in *Nature* 115, 559(1925); cf. Back and Lande, *C. A.* 19, 2454.

Fluorescent screens. S. E. SHEPPARD and L. W. EBERLIN. *Brit.* 223,568, Feb. 1, 1924. See U. S. pat. 153,782 (*C. A.* 19, 1664).

#### 4—ELECTROCHEMISTRY

COLIN G. FINE

Advances in the electrochemical industry in 1920-1924. RUDOLF MEINGAST. *Chem.-Ztg.* 49, 221-2, 313-4, 333-4, 377-8, 417-8, 446-7, 461-2, 473-4, 497-9, 533-4, 554-6, 578-9, 582, 585-8, 606-7(1925). E. H.

Some new centers of electrochemical industry. I. Electrolytic alkali and chlorine. J. B. C. KERSHAW. *Ind. Chemist* 1, 233-8(1925).—A review. E. H.

The electrochemical and electrometallurgical industries of the Pyrenees. GIRAN. *Bull. soc. franç. élec.* 4, 843-8(1924); *Science Abstracts* 28B, 126-7(1924).—G reviews the progress and developments that have been carried out since his report of 1922 on the manuf. of Zn, Al, ferro alloys, steel,  $CaC_2$ , abrasives, and synthetic  $NH_3$ . Conclusion: The most striking developments are occurring in the industrial production of metals by electrolysis. H. G.

A laboratory high-frequency vacuum furnace. J. R. CAIN AND A. A. PETERSON. *Trans. Am. Electrochem. Soc.* 48 (preprint) (1925).—A new high-frequency vacuum furnace is described which eliminates sources of contamination met with in carbon-resistor type of vacuum furnaces. The furnace is operated inside an evacuated bell jar; the base plate is bakelite; crucibles are made of  $MgO$  or zircon. The melting coil and the high-frequency generator are of the Ajax-Northrup design. C. G. F.

Electric furnace replaces converter. F. E. HINNERS. *Elec. World* 86, 374 (1925).—Expts. with a 3-ton elec. furnace show that the castings produced are equal if

not superior to those produced in the converter. Advantages claimed for the electric furnace product include: charges consist entirely of scrap, the cost is lower, the product more uniform and control of chem. analysis is better. The furnace has acid ( $\text{SiO}_2$ ) brick lining with a life of about 200 heats, while the roof has a life of about 290 heats. The max. furnace demand is 1550 kw for a temp. of  $1816^\circ$ . The 12 inch (0.3 m.) electrodes are consumed at the rate of 18 lbs. (8.06 kg.) per ton (909 kg.) of steel.

W. H. BOYNTON

Power factor in electrochemistry and electrometallurgy. BUNNEY *Bull. soc. franç. élec.* 4, 855-76(1924); *Science Abstracts* 28B, 125-6.—Inter-connection between general supply networks and hydroelectric installations serving electrochemical works offers advantages to both, but it also involves consideration of problems which are of minor importance in a private plant of small or medium capacity. In particular, the power factor of the electrochemical installation must be as high as possible. With the exception of N fixation furnaces, elec. furnaces are usually operated at low voltage with heavy current. Resistance furnaces absorbed 20,000 amps. operated at power factor 0.83, it was proposed to increase the current to 30,000 amps. in order to increase production but such a current would have involved zero power factor and therefore zero production. Characteristic curves of furnaces show that as the current is increased, the power rises for a time but then decreases rapidly owing to reduction in power factor. In attempting to increase the output, the power factor may be reduced nearly to the critical value 0.707 beyond which the power and therefore the production decrease rapidly. The power factor may be improved greatly by increasing the voltage applied to the furnace. Assuming constant reactance and constant current, the component pressure in phase with the current, and therefore the power and power factor, rise rapidly as the voltage is increased. Alternatively, the current may be reduced as the voltage is increased, so as to maintain the power at the max. permissible for the furnace; the reactive voltage drop then decreases while the component of voltage in phase with the current increases, hence the power factor rises rapidly. In America furnaces for the manuf. of  $\text{CaC}_2$  are operated at 90 volts per arc. (160 volts, 3-phase, 60 cycles), but in France potentials hardly ever exceed 40 volts. An alternative method of improving the power factor is converting the supplied energy to lower frequency; this solution may be preferable to the use of higher voltage where it is desired to avoid modifications to the furnace or where the furnace charge is of high conductivity. By the use of a synchronous motor-generator for frequency reduction, unity power factor can be maintained on the supply side, a considerable amount of power-factor correction being effected with regard to other loads if desired. Where motor-generators are used to supply low-voltage, heavy-current d. c. for electrochemical purposes, a synchronous motor should be used; for very heavy currents the set must run at relatively low speed and the power factor of induction motors with a large number of poles is low.

H. G.

Measurement of power-factor in industrial plants. R. A. LANE *Elec. J.* 22, 391-3(1925)

C. G. P.

Electrolytic preparation of pure iron. E. DUBRE *Wiss. veröffentl. Siemens-Konzern* 3, 39-42(1924)—The electrolyte consists of a cold sat'd soln. of  $\text{FeCl}_2$  contg.  $\text{MgCl}_2$  and free acid equiv. to less than 0.01 N. The anode may consist of steel or even cast Fe. The cathode is rotated inside a stationary auxiliary cathode on which a small secondary a. c. (of which the negative component is greater than the positive) is superimposed. A porous earthenware U-tube is arranged round the cathode and a current of air is blown through the tube. At the bottom of the cell a no. of permanent magnets sealed into thin glass tubes serve to collect the particles of carbide and silicide that fall from the anode. With this app. Fe of more than 99.994% purity may be prepd. from material contg. as much as 3% C, 1% Si and 0.4% P.

B. C. A.

(Nickel) Plating automobile bumper bars. T. C. EICHSTADT *Metal Ind.* (London) 26, 603(1925)—A high-grade rust-resisting Ni plate is produced by the use of a bath consisting of: 34 kg. single Ni salts, 0.68 kg. of double Ni salts, 0.23 kg.  $\text{MgSO}_4$ , 0.23 kg.  $\text{H}_2\text{BO}_3$  and 189 l. water. The c. d. is 12-15 amp./sq. ft. (11-14 amp./sq. dm.) without agitation, and 20-24 amp./sq. ft. (18-22 amp./sq. dm.) where the cathode moves and the soln. is agitated. Frequent addns. of  $\text{CdCl}_2$  and HF are needed. The bars are electrically cleaned, receive a Cu strike, are washed in water, dipped in a 6%  $\text{HCl}$  or HF dip, again washed and plated. After washing, a heavy Cu deposit is secured which when thoroughly buffed and colored requires a thinner Ni plate and less buffing for finishing.

W. H. BOYNTON

The electrodeposition of zinc from sulfate solutions. A. L. MARSHALL *Trans. Faraday Soc.* (advance proof) (July 6, 1925).—The efficiency of Zn deposition in sulfate solns. increases with rising temp. more rapidly, the lower the Zn and the higher the

acid content of the soln. Increasing temp and increasing  $\text{ZnSO}_4$  concn increase the single electrode potential of the Zn electrode (referred to the soln.). The presence of Mn retards the formation of  $\text{H}_2$ , thus increasing the efficiency while Sb decreases the efficiency. The effects of Fe, Cu, Sb and Mn on the deposition are given by curves. A Cu coulometer has been developed which can conveniently measure currents up to 15 amp. or greater.

D. S. VILLARS

Recent developments in storage batteries. P. A. FLORENSKY. *Electrichestvo* 1925, 351.—A review of the recent researches of Ch. Fery and his non-sulfating Pb battery using O as a depolarizer.

C. G. F.

Recent improvements in primary cells. FERY. *Bull. soc. franç. elect.* 4, 835-42 (1924); *Science Abstracts* 28B, 124.—After a brief historical note on the development and practical use of primary cells, F. points out some features of present-day practice. The Cu-oxide cell is increasingly used on account of the heavy and const. currents that it can supply. In recent form a Cu wire is wrapped round the Cu-oxide block to obtain a greater approximation to steady conditions at starting. The agglomerate is made up into plates which alternate with Zn plates after the manner of an accumulator. The plates can be reoxidized after exhaustion by heat treatment. The gravity and other types of Daniell cell are falling into disuse and are partly replaced by a form of cell where the O of the air acts as the depolarizer instead of  $\text{MnO}_2$ , which was difficult to obtain during the war. In this cell, due to F., the Zn plate is horizontal and at the bottom sepd by a wooden cross from the porous C tube electrode above. The electrolyte is the same as in a  $\text{MnO}_2$  cell, and sufficient O to act as a depolarizer is taken up from the air. Good constancy and small local action are obtained. A recent improvement in the dichromate battery, due to Benko, is the filtration of the chromic soln. through porous C to remove free O and to diminish local action.

H. G.

Electrical resistance of copper at high temperature. PAUL CLOKE. *Elec. World* 86, 224(1925).—Cu wire wound around a  $\text{SiO}_2$  tube was heated in an atm. of pure N and from the data obtained a table of values was made giving the resistance, the temp., actual and absolute, the log of the resistance, and the log of the absolute temp. The log of the resistance, plotted against the log of the absolute temp. gave a straight line. By the  $\Sigma - \Delta$  method, the av. slope below  $600^\circ$  was 1.049, showing that the resistance varies as  $T^{1.049}$ , which gives a simple relationship for computing resistance up to  $600^\circ$  of any Cu of commercial cond. The av. slope above  $600^\circ$  was 1.243. The exponent 1.049 gives results in close agreement with the formulas in common use for resistance computation at comparatively low temps.

W. H. BOYNTON

Corona investigation on an artificial line. M. F. GARDNER. *J. Am. Inst. Elec. Eng.* 44, 813-20(1925).

C. G. F.

The unipolarity of the corona. M. G. EVREINOV. *Electrichestvo* 1925, 284.

C. G. F.

Measuring effects of corona on rubber. F. L. HAUSHALTER. *Elec. World* 86, 267-9(1925).—Deleterious effects are produced by ozone in a very short time if the rubber is subjected simultaneously to corona and tension. The degree of cracking depends upon the time the voltage is applied. The app. employed is illus. and the effects under various conditions are shown. Unstretched rubber is little affected by corona.

W. H. BOYNTON

A high-tension bridge for measurement of dielectric losses in cables. R. W. ATKINSON. *Elec. J.* 22, 58-66(1925); cf. B. Hague, *World Power* 4, 81-3(1925).—This is a new type of a. c. bridge and is an improvement on those of Wien and of Rosen.

C. G. F.

The industrial production of Zn (CASTELL) 9. The properties and testing of magnetic materials (SPOONER) 9.

Electric resistance hearth furnace. T. F. BAILY. U. S. 1,546,534, July 21

Electric resistance furnace for melting metals covered with a salt bath. M. SPERLING. *Brit.* 228,599, Oct. 31, 1923. Furnace walls of refractory bricks may be exposed to the action of Al powder at a high temp. so that the surface of the bricks is reduced to metallic Si. The furnace may be used for coating Fe with Sn, Zn, brass or Al, with the use of salt baths to which deoxidizing agents may be added overlying the molten coating metal.

Electric resistance furnaces for heat-treatments. A. RUCKSTAHL. U. S. 1,547,000-1-2, July 21.

Electric soaking pit for ingots. T. F. BAILY. U. S. 1,546,535, July 21.

Soaking pit for treating ingots. T. F. BAILY. U. S. 1,546,533, July 21. Holes of soaking pits are lined with Si carbide or other material which will not reduce in the presence of C and elec. heating elements are located through the side walls of the holes.

Chromium alloys. W. H. SMITH and C. M. CAMPBELL. U. S. 1,545,705, July 14. Fe, Ni or other Fe group metal to be alloyed with Cr is first melted in an elec. furnace covered with a C free slag, which is elec. conductive at elevated temps., and which is sufficiently basic and refractory to prevent the arc from striking through; and the Cr component is then dissolved in the molten Fe-group metal. The slag may comprise CaO 80-90 and fluorspar 20-10%.

Apparatus for electric precipitation of suspended particles from gases, etc. R. B. RATHBUN. U. S. 1,545,975, July 14. Cf. C. A. 19, 613.

Electric battery. K. OETTL and ELTAS ELEKTRO-ARY-GES. Brit. 228,702, Jan. 29, 1924. Structural features.

Electric primary battery. E. A. G. STREET. U. S. 1,545,801, July 14. Structural features.

Dry-cell battery. S. APOSTOLOFF. U. S. 1,546,461, July 21. Structural features.

Storage battery. S. JENCKE. U. S. 1,546,541, July 21. Structural features.

Storage battery. J. M. PUCKETT. U. S. 1,545,695, July 14. Structural features.

Storage battery. R. B. OWEN. U. S. 1,546,101, July 14. Structural features.

Storage batteries. E. HANDLER. U. S. 1,546,379, July 21. Wood separators are treated with sulfite soln. to remove constituents which would be injurious in a battery. The treated separators and metal battery elements are assembled and kept together in dry condition until it is desired to prepare the battery for use.

Storage-battery separators. W. L. TOPPLE and FULLER'S UNITED ELECTRIC WORKS, LTD. Brit. 228,271, Nov. 2, 1923. Structural features.

Electroosmosis. V. A. LAPENTA. U. S. 1,546,908, July 21. An app. is described adapted for a wide variety of electroosmotic setups.

Apparatus for electrolysis of water. L. CASALE. U. S. 1,547,362, July 28. Electrodes are used with passages for the gases liberated, to facilitate their sepn. and provide for uniform cond. between the electrodes.

Apparatus for electrodeposition of metals from ores, scrap, etc. T. W. S. HUTCHINS. U. S. 1,545,561, July 14.

Brush for electroplating conductive surfaces. E. A. COADY and F. W. OLMSTEAD. U. S. 1,545,941, July 14.

Brush for electroplating conductive surfaces. F. CONLIN. U. S. 1,545,942, July 14.

Generating gases electrolytically under pressure. P. HAUENWEISTER. Brit. 228,231, Oct. 23, 1923. A pressure which is a "multiple of atm. pressure" is constantly maintained to avoid varying soln. and release of gases which would occur with variations of pressure.

Electrolytic cleaning of "stainless" iron and steel. T. RONDELLI. Brit. 228,278, Nov. 6, 1923. Articles of Fe or steel which may contain Co, Ni and Cr are subjected as anodes to a strong hot soln. of caustic alkali and after this are treated with dil. acid to produce a bright white metal surface.

Leading-in wires for incandescent lamps, etc. S. L. HOYT. U. S. 1,547,394, July 28. Composite low-expansion leading-in wires comprise a core composed of any alloy of Fe and Ni and a covering of Cu. The % of Ni in the core is greater near the Cu covering than at the center of the core, which serves to facilitate bonding of the core and Cu. U. S. 1,547,395 specifies a Ni-coated wire.

## 5—PHOTOGRAPHY

C. E. K. MEES

Contributions to our knowledge of the action of light on silver bromide. H. STOCK. *Z. wiss. Phot.* 23, 132-6 (1923).—This is a criticism of the recent article by R. Strömberg (C. A. 17, 3818) on the action of light on AgBr. Strömberg's method of preparing a AgBr film by treating a Ag film on glass with Br vapor is not such as would effect a quant. bromination and the unchanged Ag would tend to retain such Br as might be liberated in the subsequent insolation. The light source was not specified, and there did not appear to have been any attempt to vary the insolation widely, nor was its amt. considered with respect to solarization. Strömberg did not specifically show that his films were light-sensitive. His result, therefore, that no weighable amt. of Br is liberated from AgBr by the action of light, is not conclusive.

C. E. K. MEES

The history and theory of the latent image. II. LÜPPO-CRAMER. *Z. wiss. Phot.* 23, 122-32(1925); cf. *C. A.* 19, 1230.—L.-C.'s view that the latent image consists in part of "soluble," or free, Ag, and in part of Ag that is "insoluble" (occluded, or adsorbed), is applied to the interpretation of the Albert and Lainer effects and of many facts of theoretical interest that have more recently entered into the history of photography. C. E. K. MEES

Latent fog. LÜPPO-CRAMER. *Z. wiss. Phot.* 23, 184-200(1925); cf. *C. A.* 19, 18.—L.-C. discusses broadly and at some length the general subject of latent fog. Much of his recent exptl work is included, but in addition to this and to the description of the work of others and to the general theoretical discussion there does not appear to be anything entirely new. The manifold nature of latent fog is emphasized. The author designates as *secondary fog* all such developable impressions as cannot be traced to the action of radiant energy. This appears to correspond with what is usually denoted by the *Russell effect*, and approx. with the *actinautography* of Kahlbaum (1905). C. E. K. MEES

Developable influences of pressure on the photographic emulsion. P. WULFF. *Z. wiss. Phot.* 23, 145-8(1925)—W describes, and illustrates with figures, the effect of non-shearing and of shearing pressure before exposure, and of shearing pressure after exposure, in the cinematograph positive film. The non-shearing pressure was obtained by means of a pointed object through an interposed sheet of celluloid, and the shearing pressure by its direct application to the emulsion film. The exposure was to white light through an Eder-Hecht tablet. The effect of pressure without shear is simply a reduction in sensitivity, no latent fog being produced. Shearing pressure, on the other hand, produces latent fog. Regarding this, the old explanation of a removal of gelatin from the surface of the Ag halide grains is cited, but no explanation is suggested for the reduction in sensitivity by simple pressure. C. E. K. MEES

Ripening of washed gelatin emulsions and the influence of foreign substances. ANON. *Phot. Ind.* 1925, 372-3.—Factors which tend to increase sensitivity of an emulsion during ripening are outlined. Various substances may be added to the ripened emulsion, such as alum or formalin, for hardening, glycerol to prevent over-drying, etc. Traces of Cu or Hg salts greatly decrease sensitivity. M. L. DUNNON

Characteristics of photographic sensitizers and distortions on plates due to local desensitizing. FRANK E. ROSS. *Astrophys. J.* 61, 337-52(1925)—See *C. A.* 19, 939. E. H.

Influence of washing on the action of desensitizers. RESEARCH LABORATORY, PATHÉ CINEMA. *Brit. J. Phot.* 72, 410-1(1925).—With successive washings undeveloped desensitized plates are partially restored to their original sensitiveness. Plates treated with a 0.01% soln. of pinakryptol green for 2 min. were least affected, returning to about  $\frac{1}{2}$  their original speed. In treatment with a soln. of 0.005% sky blue rhodulin and 0.015% acridine yellow, the washing test gave a final sensitiveness of about  $\frac{1}{4}$  the original speed; with 0.01% phenosafranin about  $\frac{1}{4}$  the original speed. With dyes which fog and desensitize at the same time the treated plates showed practically no reduction in fog after extensive washing. G. E. MATTHEWS

Reduction of negatives by means of permanganate with acetic acid. R. NAMIAS. *Il. prog. fot.* 32, 185-8(1925)—Negatives may be reduced by converting the surface image into AgBr and removing the underlying Ag with acid  $\text{KMnO}_4$ , this tending to give negatives of softer quality, but a difficulty arising from this process is that the soln. of  $\text{KMnO}_4$  and  $\text{H}_2\text{SO}_4$  is reduced by the gelatin and deposits  $\text{MnO}_2$  in it. It is now suggested that  $\text{AcOH}$  should be substituted for the  $\text{H}_2\text{SO}_4$ , this procedure greatly reducing the deposition of  $\text{MnO}_2$ . The negative can be bleached on the surface with bromide and ferricyanide until only the highlights remain on back of the negative, and these can be removed by treatment with 0.5% soln. of  $\text{KMnO}_4$  contg. 2.5% of glacial  $\text{AcOH}$ . The final clearing is effected as usual in a bisulfite bath. C. E. K. MEES

Contribution to the knowledge of luminography. L. VANINO AND S. ROTHSCHILD. *Chem.-Ztg.* 49, 545-6(1925).—Direct contact negatives may be made of illustrations in books, etc., by means of this process. A plate covered with luminous paint is used as a light source. If the page on which the cut appears has no printing on the back, the following procedure is used: The luminous plate is exposed to the light for 1 min. to activate it. It is then placed face up behind the copy. A photographic plate, film, or paper is placed over the copy with the emulsion side down. The book is then closed, weighted and allowed to remain 5-15 min. The photographic plate is then removed and developed in an ordinary developer. If the page has printing on the reverse side, it is backed with black paper and the photographic plate is placed over the cut as before, but the luminous plate is placed, luminous side down, over the photographic plate.

In this case a hard working developer is used. Advice is given regarding suitable photographic plates, etc. Illustrations are given of cuts reproduced by this means.

MERRILL W. SEYMOUR

Raw materials of photographic and cinematographic films. I. ANON. *Phot Ind* 1925, 747.—A photographic film must be transparent, colorless, tough, elastic, stable, and resistant to water and photographic solns. The only substances which are known to fulfil these conditions are cellulose nitrate and cellulose acetate. Nitrocellulose and especially esters of partially decomposed cellulose, decompose in the presence of alkalis or acids and eliminate oxides of N, which fog emulsions. Cellulose acetates have a 45-55%  $\text{HC}_2\text{H}_3\text{O}_2$  content. Their solvents are  $(\text{CH}_3)_2\text{CO}$ , methyl acetate, methyl formate, etc., and several other substances may be added. With cellulose nitrate, camphor is used, but with the acetate, triphenyl phosphate and hexachloroethane are used. In laminated films the percentage of camphor can be decreased on the emulsion side and the different layers can be varied otherwise. A thin emulsion of hardened gelatin with  $\text{CaCl}_2$  or  $\text{BaCl}_2$  increases the elec. cond. and diminishes static. Non-curling property is given by coating the back with gelatin, shellac, or in the case of an acetate film, with a mixt. of cellulose acetate and 1% of the  $\text{H}_2\text{O}$ -sol. mono- or di-acetin. Inflammability can be decreased by adding to nitrocellulose films gypsum in combination with triphenyl phosphate or by overcoating with a mixt. of water glass, glycerol and gum arabic.

M. L. DUNN

Artificial white light for photographic purposes. H. NAUMANN. *Phot J.* 65, 348(1925).—In a previously published formula (*C. A.* 19, 2458), the ultra-violet transparency was defective because of the use of toluidine blue. This is corrected by the substitution of thionine blue.

K. C. D. HICKMAN

Color photography. E. SENIOR. *J. Soc. Dyers Colourists* 41, 250-1(1925).—An illustrated lecture

L. W. RIGGS

Dichromate photographic process. W. H. WADHAM, A. ZIEHM, H. A. SONDERMANN and P. WORTHE. *Brit.* 228,377, March 14, 1924. The sensitiveness of colloid layers contg.  $\text{K}_2\text{Cr}_2\text{O}_7$  is increased by the addition of "base metal compds." such as  $\text{MgCl}_2$ ,  $\text{NiCl}_2$ , or  $\text{MnSO}_4$ , and acid Na phosphate or other acid salt. Chlorides of Fe and Cu are less effective. Aniline HCl may also be used as a sensitizer.

Colored powders for "dusting on" in photography. E. BURI. *Brit.* 228,187, Jan 25, 1924. A powder suitable for dusting on partly dried exposed sensitized gelatin paper to effect a selective coloring comprises peat, lycopodium, charcoal, mineral colors, etc., naturally contg. (or treated with) resin or wax.

## 6—INORGANIC CHEMISTRY

A. R. MIDDLETON

Quadrivalent lead. J. ŠTERBA-BOEHM and MISS M. AUERSPERGROVA. *Rec. trav. chim.* 44, 390-9(1925).—The purpose of this work, i. e., the prepn. of Pb disulfide was not attained. The reaction between  $\text{PbO}_2$  and  $\text{H}_2\text{S}$  gas gives rise to a heterogeneous mass contg. besides unchanged  $\text{PbO}_2$ , a little S and  $\text{PbSO}_4$ . When the air is removed with  $\text{CO}$ , the reaction is slow and incomplete even up to  $150^\circ$ . Two reactions probably take place in one of which PbO and S are formed and in the other PbS and S. As the temp. rises to  $90-100^\circ$  and above, the latter reaction predominates. In liquid  $\text{H}_2\text{S}$  at ordinary pressures  $\text{PbO}_2$  reacts to give more free S and less PbS so that the 1st reaction seems to predominate. Even under these conditions the reaction is incomplete.  $\text{K}_2\text{S}$  in  $\text{H}_2\text{O}$  soln. reacts slowly and incompletely with  $\text{PbO}_2$  at ordinary temps. and PbS is probably formed.  $\text{H}_2\text{S}$  gas acting on a soln. of  $\text{PbCl}_2$  in MeOH gives only  $\text{PbCl}_2$ . The results show that  $\text{PbS}_2$  is little stable or rather incapable of existing. This is comparable with what was found with  $\text{PbI}_2$  and  $\text{PbBr}_2$  and shows a great tendency of  $\text{Pb}^{IV}$  ions to be reduced to  $\text{Pb}^{++}$  and likewise of  $\text{S}^{--}$  to be oxidized to S.

E. J. WITZEMANN

Lead borates. E. C. BROWN and J. R. PARTINGTON. *J. Soc. Chem. Ind.* 44, 325-6T(1925).—Methods used by earlier workers to prep. Pb borates by fusion and pptn. were tried out, but no positive evidence was obtained for the existence of a simple borate of Pb. The (1) occlusion of  $\text{Pb}(\text{NO}_3)_2$  by the ppt., and (2) the effect of washing, are important factors. Such borates of Pb as have been described are really basic substances whose compn. depends upon the method of prepn.

W. C. E.

Spectrographic study of the formation of mercuric complexes. P. JOB. *Compt.*

*rend* 180, 1932-4(1925)—Mixts. of equimolal solns. of  $\text{HgCl}_2$  and  $\text{KBr}$  give a very marked absorption max. corresponding to  $\text{HgCl}_2 \cdot 4\text{KBr}$ , and this max. compn. does not vary with a change in the concn. The reaction:  $\text{HgCl}_2 + 4\text{KBr} = \text{HgBr}_4\text{K}_4 + 2\text{KCl}$  is the only plausible reaction scheme. The equil. const.  $[K = C_{\text{HgBr}_4\text{K}_4} C_{\text{KCl}}^2 / C_{\text{HgCl}_2} C_{\text{KBr}}^4]$  is equal to  $1.5 \times 10^{-4}$ . The same reaction with  $\text{KI}$  gives an equil. const. of about  $10^{-4}$ . In a study of this complex formation by the action of  $\text{KBr}$  on acid solns. of mercuric sulfate or nitrate, the absorption curves show not only a max. corresponding to the ion  $\text{HgBr}_4$  but also a marked min. corresponding to  $\text{HgBr}_2$ . This compn. remains nearly invariable when non-equimolal solns. are used. J. H. P.

A contribution to the knowledge of hydrolytic cleavage of magnesium chloride solutions. C. G. SCHWALBE AND RUDOLF SCHEFF. *Ber* 58B, 1354-5(1925).—The present investigation is a quant. supplement of the previous observation of the authors (*C. A.* 18, 3047) that  $\text{MgCl}_2$  accelerates the hydrolysis of cellulose, a process accompanied by evolution of  $\text{HCl}$ . It was impossible to deduce from this earlier work whether the  $\text{HCl}$  formed is a product solely of  $\text{MgCl}_2$ , or whether various salts such as sulfites,  $\text{MgSO}_4$ ,  $\text{NaCl}$  and  $\text{CaCl}_2$  facilitate decompn. In sep. expts.  $\text{MgCl}_2$  solns. were heated in an autoclave at  $150^\circ$ , and various quantities of sulfite and other inorg. salts were added. Under these conditions no  $\text{HCl}$  was formed. When, however, 100 g. of sulfite-cellulose was added, 0.66 g. of  $\text{HCl}$  was produced. Plant fibers clearly accelerate the hydrolytic cleavage of the  $\text{MgCl}_2$  mol. This work confirms the conclusion of Ristenpart (*C. A.* 6, 1530) that an aq. soln. of  $\text{MgCl}_2$  does not decompose at temps. less than  $106^\circ$  even in the presence of a current of air.

H. R. MOORE

The precipitation of ferric salts with ammonium sulfide. HENRY KREPELKA AND WILLIAM POUROUZEK. *Rec. trav. chim.* 44, 416-24(1925).—The early history of this problem is reviewed. The compn. of the ppt. formed from  $\text{Fe}^{+++}$  salt solns. by  $(\text{NH}_4)_2\text{S}$  depends on the concn. of  $\text{H}^+$  ions in the medium. Concd.  $\text{Fe}^{+++}$  salt solns. and very dil.  $(\text{NH}_4)_2\text{S}$  give a mixt. of  $\text{FeS}$  and  $\text{S}$ . Very concd. solns. of  $(\text{NH}_4)_2\text{S}$  and dil.  $\text{Fe}^{+++}$  salt solns. lead to  $\text{Fe}_2\text{S}_3$ . Under ordinary analytical conditions a mixt. of  $\text{FeS}$ ,  $\text{FeS}_2$ , and  $\text{S}$  is usually formed.  $\text{Fe}_2\text{S}_3$  is unstable in neutral medium and undergoes the reaction:  $\text{Fe}_2\text{S}_3 \rightarrow \text{FeS} + \text{FeS}_2$ . The free  $\text{S}$  of the ppt. cannot be extd. in stoichiometric amt. because of the presence of  $\text{H}_2\text{O}$  (probably  $\text{H}_2\text{O}$  of hydration). The ppt. is not a salt of some thioferric acid since all of its  $\text{NH}_3$  can be removed by thorough washing; the ppt. then becomes insol. in  $\text{KOH}$ .

E. J. WITZEMANN

Investigations on solutions of mannito-aluminates. P. HERASYMENKO. *Rec. trav. chim.* 44, 435-6(1925).—In the presence of polybasic alics.  $\text{Al}(\text{OH})_3$  is not pptd. by alkali from the soln. of an  $\text{Al}$  salt. The aim of this work was to investigate the nature of complexes formed by mannitol in aq. solns. of aluminates. Complex compds. of  $\text{Al}(\text{OH})_3$  with hydroxy acids and polybasic alics. were investigated by Hanuš and Quadrat (*C. A.* 4, 298) but they did not succeed in proving the formation of complexes between polybasic alics. and aluminates because of the small  $\text{OH}^-$  ion concn. of the  $\text{NH}_4\text{OH}$  solns. used as  $\text{H}$ . has now detd. in this work. The exptl. facts developed show that several complexes can be formed by the interaction of mannitol with aluminates and  $\text{OH}^-$  ions. When the changes in the f. p. ( $\Delta f_0 - \Delta f$ ) are plotted against the total concn. of added mannitol in soln. most of the curves have a max., and from the position of these the amt. of mannitol used in the mol. of the complex can be detd., since further additions of mannitol produce almost normal depressions of the f. p., thus showing that the complexes are already satd. with mannitol. The data indicate that the first additions of mannitol to an aluminate soln. give rise to a complex dibasic anion with  $\text{OH}^-$  and aluminate ions, the most simple form of which is  $[\text{Al}(\text{OH})_2 \cdot \text{M}(\text{OH}^-)_2]$  ( $\text{M}$  = mannitol). At the same time a less complex and monobasic anion  $[\text{Al}(\text{OH})_2 \cdot \text{M}(\text{OH}^-)]$  must arise as is evident from the exptl. data. As soon as the additions of mannitol are not all used up in building the complex the max. appears. At the max. the amt. of mannitol added will correspond to half the sum of the concn. of aluminate and  $\text{OH}^-$  ions, as was actually observed. When the soln. contains excess  $\text{OH}^-$  ions over the aluminate ions, then the complex formation requires much more mannitol. Here it must be assumed that a complex compd. is formed in greater quantity, which for 1 equiv. of aluminate contains more mannitol as well as more  $\text{OH}^-$  ions. Cond. detns. in  $\text{NH}_4\text{OH}$  solns. showed that the acidity of the complex mannito-aluminic acid is about  $3 \times 10^{-10}$ .

E. J. W.

Addition compounds between stannic iodide and organic bases. G. SCAGLIARINI. *Atti. accad. Lincei* [6], I, 582-6(1925).—The halogen compds. of  $\text{Sn}^{IV}$ , particularly  $\text{SnCl}_4$  and  $\text{SnBr}_4$ , easily give complexes through secondary valences. Thus Pfeiffer (*Ann.* 376, 285) obtained  $\text{SnCl}_4 \cdot 2\text{BzH}$  and  $\text{SnBr}_4 \cdot 2\text{BzH}$ . In these compds. the general formula is  $\text{RACO-SnX}_4\text{-COR}$ , in which  $\text{R}$  is a  $\text{Ph}$  or  $\text{C}_6\text{H}_5\text{OH}$  group and  $\text{A}$  is  $\text{Me}$  or  $\text{NH}_2$ . Complexes of  $\text{SnI}_4$  are, however, little known. A cold satd. soln. of hexa-

methylenetetramine (I) in  $\text{CHCl}_3$  treated drop by drop with a cold satd. soln. of  $\text{SnI}_4$  in  $\text{CHCl}_3$  gave a white microcryst. ppt. of a complex  $\text{SnI}_4 \cdot 5\text{C}_4\text{H}_{12}\text{N}_4$  (in the Wernerian form  $[(\text{C}_4\text{H}_{12}\text{N}_4)_5\text{SnI}_4]$ ), which was washed with  $\text{CHCl}_3$  but could not be recrystd. If an excess of  $\text{SnI}_4$  is added the ppt. becomes yellow. It may be whitened by adding more I. If the soln. of I is added drop by drop to the soln. of  $\text{SnI}_4$  violet microcrystals of a complex  $\text{SnI}_4 \cdot 4\text{C}_4\text{H}_{12}\text{N}_4 \cdot 2\text{CHCl}_3$  (or  $[(\text{C}_4\text{H}_{12}\text{N}_4)_4\text{Sn}(\text{CHCl}_3)_2]$ ) are formed. If excess I is added the ppt. becomes yellow and then white. The violet ppt. was filtered off, washed with  $\text{CHCl}_3$  and analyzed. Because of the insol. of these complexes no tests could be made to det. if the I is in the external sphere. The violet complex remains unchanged *in vacuo* over  $\text{H}_2\text{SO}_4$  at  $80^\circ$ , but in humid air it is rapidly decolorized and loses  $\text{CHCl}_3$ . Similar effects were observed by Rastelli (C. A. 19, 2192) with aldehyde phenylhydrazones in  $\text{CHCl}_3$ ,  $\text{CHBr}_3$  and  $\text{CCl}_4$  solns. The colored solns. are also decolorized in moist air. The mechanism of this phenomenon is discussed briefly.

E. J. WITZEMANN

A new process of separation of aliphatic amines from ammonia. P. LEONE. *Gazz chim ital* 55, 246-52 (1925).—Existing methods of sepg.  $\text{NH}_3$  from amines are reviewed. All methods available leave something to be desired. Some are based on solubility in abs.  $\text{EtOH}$  or  $\text{CHCl}_3$  and do not give exact results; others like the method of Quantin (*Compt rend* 115, 561) are limited in application to some amines while that of Francois (*Compt rend* 114, 567) cannot be used when a little  $\text{NH}_3$  is present. L. observed that Na cobaltinitrite ppts  $\text{NH}_3$  from solns. of primary, secondary and tertiary amines quantitatively under suitable conditions and that this reagent may be used to det.  $\text{NH}_3$  present or to purify these compds. The reagent used was a soln. of pure  $\text{Na}_2\text{Co}(\text{NO}_2)_6$  in  $\text{EtOH-H}_2\text{O}$  containing an equal wt. of  $\text{NaNO}_2$ . To test for  $\text{NH}_3$  in a soln. of amine an excess of this reagent was added to the aq. soln. A ppt. or even a turbidity indicates the presence of  $\text{NH}_3$ . In order to det. the amt. of amine present in a mixt. of amine and  $\text{NH}_3$ , salts a detn. of total volatile alkali was made. Then about 0.5 of the calcd. amt. of the Co reagent was added. After 24 hrs. the ppt. was filtered off and the volatile alkalinity was again detd. by distilling an aliquot portion with excess  $\text{NaOH}$ . When  $\text{NH}_3$  is to be removed from a soln. of amine it is neutralized with  $\text{AcOH}$  and treated with the Co reagent. Excess  $\text{NaOH}$  is added to the filtrate and the soln. is distilled. The distillate is rigorously free from  $\text{NH}_3$ .

E. J. WITZEMANN

Nitrogen tetrasulfide and nitrogen tetraselenide. H. B. VAN VALENBURGH AND J. C. BAILLAX, Jr. *J. Am. Chem. Soc.* 47, 2134-7 (1925).—A stream of dry  $\text{NH}_3$  was passed through 5 cc. of  $\text{S}_2\text{Cl}_2$  dild with  $\text{Et}_2\text{O}$  to 150 cc. The reaction is  $16\text{NH}_3 + 6\text{S}_2\text{Cl}_2 = 12\text{NH}_4\text{Cl} + \text{N}_2\text{S}_4 + 8\text{S}$ . The ppt. is extracted with  $\text{Et}_2\text{O}$  and the extract allowed to evap. in air leaving orange yellow crystals of strong characteristic odor. Yield 65%. Yield was much poorer when  $\text{C}_6\text{H}_6$  or  $\text{CS}_2$  was used as solvent.  $\text{N}_2\text{Se}_4$  was prepd. similarly but yields were better with  $\text{CS}_2$  as diluent and a more dil. soln. The mol. wts. were detd. and found to correspond to the formulas above. The hydrolysis products of  $\text{N}_2\text{S}_4$  were found to be  $\text{H}_2\text{S}$ ,  $\text{SO}_2$ ,  $\text{S}$  and  $\text{NH}_3$ . By passing  $\text{NH}_3$  more than 0.5 hr. through  $\text{S}_2\text{Cl}_2$  in  $\text{Et}_2\text{O}$  or through  $\text{N}_2\text{S}_4$  in  $\text{Et}_2\text{O}$ ,  $\text{C}_6\text{H}_6$  or  $\text{CS}_2$  or  $\text{N}_2\text{Se}_4$  in  $\text{CS}_2$ , dark red liquids were obtained which on evapn. left heavy viscous liquids which did not lose  $\text{NH}_3$  on heating. Mol. wt. and analytical data could not be decisively interpreted.

A. R. MIDDLETON

New oxide of nitrogen, nitroso-nitrogen trioxide, and its bearing on the oxidation of nitric oxide. R. L. HASCHE. *J. Am. Chem. Soc.* 47, 2143-8 (1925); cf. C. A. 19, 1980.—The green compd. formed by action of  $\text{NO}$  on  $\text{O}_3$  at liquid-air temps. was prepd. and analyzed and found to have the formula  $(\text{N}_2\text{O}_4)_2$ . The green compd. decomps. just above the b. p. of  $\text{O}_3$  leaving powdery, blue  $\text{N}_2\text{O}_4$  (Helbig, *Ann. acad. Lincei* 5, 166 (1903)). H.'s analysis was confirmed. The instantaneous formation and extreme instability of  $\text{N}_2\text{O}_4$  indicate that it is a peroxide. The following reactions are considered probable.  $\text{O}_3 + 2(\text{NO})_2 \rightarrow \text{N}_2\text{O}_4 \cdot \text{di-trinitrosyl peroxide}$ . At somewhat higher temp.,  $\text{O}_3 + 2(\text{NO})_2 \rightarrow \text{N}_2\text{O}_4 \cdot \text{di-dinitrosyl peroxide}$ . In the gas phase,  $\text{O}_3 + 2\text{NO} \rightarrow \text{N}_2\text{O}_4 \cdot \text{dinitrosyl peroxide}$ . In decompn.,  $\text{N}_2\text{O}_4 \rightarrow 2\text{NO}_2$ ;  $\text{N}_2\text{O}_4 \rightarrow 2\text{N}_2\text{O}_3$ ;  $\text{N}_2\text{O}_4 \rightarrow 2\text{N}_2\text{O}_2 + 2\text{NO}$ . A sketch of the app. used for prepn. and analysis is included.

A. R. MIDDLETON

Preparation of nitric oxide from sodium nitrite. W. A. NOYES. *J. Am. Chem. Soc.* 47, 2170 (1925).—Nearly pure  $\text{NO}$  is obtained by dropping concd.  $\text{H}_2\text{SO}_4$  into  $\text{NaNO}_2$  covered with 2-3 times its wt. of water. The small content of  $\text{NO}_2$  is removed by passing the gas through concd.  $\text{H}_2\text{SO}_4$  or by collecting it over water.

A. R. M.

Attempt to prepare nitro-nitrogen trichloride. III. Failure to obtain a compound containing only nitrogen and chlorine from oxides of nitrogen. W. A. NOYES. *J. Am. Chem. Soc.* 47, 2159-64 (1925); cf. C. A. 7, 2522; 16, 352.—Expts. are described

involving the action of  $N_2O_5$  on  $PCl_5$  at  $-18^\circ$  and at  $-70$ – $80^\circ$ . The products were condensed by liquid air and sepd. for analysis by fractional distn. Full details and a sketch of the app. are given. Besides the products reported by Geuther and Michaelis (*Ber.* 4, 766(1871)),  $N_2O$  was found. A brief summary of the various expts is given which have extended over 12 yrs and from which N. is forced to the conclusion that "when N and O atoms sep. the N atom has a greater affinity for another N atom than it has for Cl. Apparently only N in the form of  $NH_3$  or of one of its derivs can be induced to add Cl and split off HCl, leaving the Cl combined with the N."

A. R. MIDDLETON

The imide group. E. OLIVIERI-MANDALA *Gazz. chim. ital.* 55, 271-9(1925) — A recent paper by Schmidt (*C. A.* 18, 2868) gives O-M. occasion to review his work on the reactions with diazomide and their mechanism (*C. A.* 7, 2934; 11, 1608; 13, 844; 17, 1642). No new experimental data are given in this paper.

E. J. WITZEMANN

## 7—ANALYTICAL CHEMISTRY

WILLIAM T. HALL

Microchemistry as an industrial economy. WM. H. GESELL AND M. A. DITTMAR *Ind. Eng. Chem.* 17, 808-9(1925) — Savings in time, materials, and app. are possible by the application of micro-methods to industrial control analyses. Comparative results for micro and macro detns. of ash in drugs, menthol and menthyl acetate in oil of peppermint, Kjeldahl N in ext. of beef, and purity of alkali salts of org. acids are given, the agreement being excellent. The methods are not described. WM. B. PLUMMER

A method of general applicability in elementary analysis in the wet way. G. VORTMANN. *Z. anal. Chem.* 66, 272-5(1925) — To det. C, H and O in org. substances heat it with a known wt. of  $KIO_3$  and  $H_2SO_4$  (cf. Sterbinger, *C. A.* 13, 3112) and collect the  $CO_2$  evolved in soda lime (cf. Messinger, *Z. anal. Chem.* 29, 605; 31, 217; Simonis and Thies, *C. A.* 6, 3381). After the oxidation, titrate the excess iodate. Details of the computation are explained with anthracene, tartaric acid, and cinnamic acid as typical substances. W. T. HALL

Determination of cyanides and the use of benzene as an indicator in iodometry. NAOTOSUNA KANŌ *Sci. Repts. Tohoku Imp. Univ.* 14, 101-7(1925). — The use of benzene as a solvent for  $I_2$  is advocated for iodometric titrations. W. T. H.

Application of liquid amalgams to volumetric analysis. I. Estimation of molybdenum, titanium and iron. TAMAKI NAKAZONO *Sci. Repts. Tohoku Imp. Univ.* 14, 109-17(1925). — See *C. A.* 16, 1543. W. T. H.

Quantitative analysis of alloys containing tin, particularly Babbitt metal. HERNRICH BULTZ. *Z. anal. Chem.* 66, 257-72(1925) — Treat 1-1.5 g. of alloy in a porcelain casserole with 12-15 cc. of concd.  $HNO_3$  added in small portions. After the violent reaction is over, rinse off the cover-glass with  $HNO_3$ , replace it on the casserole and evap. to dryness. Heat the residue gently but not enough to decompose nitrates. If considerable Pb is present, it may be necessary to repeat the  $HNO_3$  treatment to make sure that all of the Sn is completely oxidized. Triturate the mass to powder with a glass rod, and mix it with 8 times as much  $Na_2S \cdot 9H_2O$ . Heat gently till the sulfide melts but not enough to expel all  $H_2O$ . Cool somewhat and add 10-15 cc. of concd.  $NH_4OH$  which has been satd. with  $H_2S$  and treated with 1-2 g. of  $Na_2S \cdot 9H_2O$ . Heat till the soln. no longer smells of  $NH_3$ . In this way sol. thio salts of Sn and Sb are obtained. Filter and det. Sb and Sn by the Clarke method as modified by Henz. Dissolve the insol. sulfide residue in  $HNO_3$  and det. Cu, Pb, etc. in the usual way. Directions are given for the making of an asbestos box for heating  $Sb_2S_3$  in a current of  $CO_2$ . For the volumetric detn. of Sn and Sb in these alloys, the following procedure has proved excellent. Treat 1 g. of alloy with 20 cc. of hot, concd.  $H_2SO_4$ . Heat till the alloy is all dissolved and  $SO_2$  removed. Add 50 cc. of water and 5 cc. of concd. HCl. For the Sb detn. add 1 drop of 0.1% methyl orange soln. and titrate with 0.1 N  $KBrO_3$ . After the titration, filter off and weigh any  $PbSO_4$ . On account of the HCl present the result will be 0.2% too low for Pb. To the filtrate from the  $PbSO_4$  (100 cc.), or an aliquot part if more than 30% Sn is present, contained in a 1-l. flask which is fitted with a Contat-Gockel valve contg. satd.  $NaHCO_3$  soln., add 20 cc. of concd. HCl and 8 g. of sheet Zn cut into strips. Keep the soln. cold by immersing the flask in water. After 20-25 min. all of the Zn should be dissolved and the Sn left as metal. Rinse down the sides of the flask, add 4 g. more of Zn and replace the valve. After 20 min., when of this Zn has not dissolved, add 70-80 cc. of concd. HCl and heat very carefully till

all of the Sn has dissolved, which will require about 30 min. Sb and Cu will remain undissolved. When no more bubbles of  $H_2$  arise, cool under the tap, rotating the soln. toward the last. Some of the bicarbonate soln. will be sucked into the flask. Remove the valve and rinse down the sides of the flask with a soln. of 0.2 g. of KI, 5 cc. of starch soln. and 10 cc. of dil. HCl in 100 cc. of water, and add a little more  $NaHCO_3$ . Titrate at once with 0.1 N  $KBrO_3$  till a blue end point is obtained. It is best to carry out a preliminary titration and in the final analysis add the indicated vol. of  $KBrO_3$  all at once.

W. T. HALL

Methods for the determination of manganese in alloy steels with particular attention to the silver-nitrate-persulfate method. A. KROFF *Chem.-Ztg.* 49, 537-9(1925); cf. C. A. 19, 2617.—For materials contg. more than about 12% Mn, the following modification of the Volhard method is recommended. Treat 1 g. of finely divided substance with 50 cc. of 6 N  $HNO_3$  and complete the oxidation with 5 g. of  $BaO_3$  or  $(NH_4)_2S_2O_8$ . Add 20 cc. more of  $HNO_3$  and evap. to small vol. Transfer to a 1. flask and treat with ZnO as usual. Make up to the mark and use 100-cc. portions for the titration with  $KMnO_4$ . Use a trial portion for a preliminary titration in every case and for the actual detn. add the indicated vol. of  $KMnO_4$  at once before attempting to get the end point. Standardize the  $KMnO_4$  against a soln. of known Mn content. For most alloy steels except those contg. considerable Co, it is well to carry out the ZnO treatment as in the Volhard method and det. Mn in the filtrate by the persulfate method. If Ni is present use a Mn-free Ni soln. similarly treated for comparison at the end point. If much Co is present, it is best to ppt. the Mn by treatment with  $KClO_3$  in  $HNO_3$  soln., as in the Ford-Williams method and dissolve the ppt. in an acid soln. of a ferrous salt before applying the persulfate method.

W. T. HALL

Determination of thorium X. P. GAZZONI *Compt. rend.* 179, 963-5(1924).—The pptg. reagent used for other substances which may be present is either  $H_2O_2$  or  $NH_3$ ; both leave the Th X in soln. but accompanied in the former case by its active deposit. The Th X is in part carried down by the ppt. and 4 or 5 pptns. are necessary to effect a good sepn.; this is more difficult when  $H_2O_2$  is used. The vessels contg. the original mixt. and the Th X, evapd. to dryness, are compared in an ionization chamber protected by Pb. The results obtained for the Th X are modified by the factor 0.88, which is calcd. from the increase and subsequent decrease of the radiation from the sepd. product, which attains a max. after 250 days.

B. C. A.

The separation of small quantities of calcium from large quantities of magnesium. V. RÖDT AND E. KINDSCHER. *Chem.-Ztg.* 49, 581(1925); *Abstr. Ibid.*—A polemical discussion as to the merits of the oxalate method for sepg. Ca from Mg. Cf. C. A. 19, 946, 2615.

W. T. HALL

Estimation of phosphorus. H. BURTON SMITH *Chem. Age* (London) 13, No. 316 (Met. Sec.) 3(1925).—Evap. the  $HNO_3$  soln. to dryness and baking the residue is recommended for accomplishing the complete oxidation of the P from a sample of steel, and instead of titrating in the phosphomolybdate method it is preferred to dissolve it in dil.  $NH_4OH$  and evap. the soln. to dryness. After baking the residue on the hot plate, it can be assumed to contain 1.65% of P.

W. T. HALL

Electroanalytical determination of cadmium in sulfuric acid solutions. E. BÜTTGENBACH *Z. anal. Chem.* 65, 452-5(1924).—The conditions recommended are: 0.2 g. Cd in 150-200 cc. of  $H_2SO_4$  soln. which is treated with NaOH till a permanent turbidity results and given the desired acidity by adding 6 g. of  $KHSO_4$ ; electrolysis for 40 min. at 3-8 volts and stirring at the rate of 300 r. p. m.

W. T. HALL

Determination of traces of carbon monoxide in air by the blood method and general considerations on the absorption of carbon monoxide by hemoglobin in the absence of oxygen. M. NICLOUX *Bull. soc. chim.* 37, 760-70(1925); cf. C. A. 19, 2615.—Full details of the method are given here.

W. T. HALL

The industrial dust problem. III. Comparative field studies of the Palmer apparatus, the konimeter and the impinger methods for sampling aerial dust. I. GREENBURG *U. S. Pub. Health Repts.* 40, 1591-603(1925).—Owing to large and variable control errors, the sugar-tube method of dust analysis cannot be recommended for use in ordinary industrial environments. The Palmer app. is satisfactory on this score but not very efficient. In air of very low dust content, the impinger gives the highest counts, averaging 22 times that of the Palmer app. and over 1.6 times that found by the konimeter. In the usual dusty workshop, the konimeter yields the highest counts, over 7.5 times that of the Palmer and 1.5 times that of the impinger. In a very dusty atm. the impinger ranks first, yielding counts 125 times that obtained by the konimeter and 7.35 that of the Palmer method. For studies of atm. of low or medium dust content, where the desideratum is to establish the condition of the atm. as quickly as

possible, the konimeter is to be recommended. The impinger is recommended for all intensive dust studies. W. T. H.

**Iodometric determination of methylene blue.** T. SABALITSCHKA AND W. IRDMANN. *Chem.-Ztg.* 49, 561(1925).—When treated with an excess of  $I_2$  in  $KI$  soln., methylene blue absorbs 4 atoms of  $I$ ; the excess  $I_2$  can be titrated with  $Na_2S_2O_4$ . No indicator is necessary as the thiosulfate begins to react with the ppt. at the end point and the dyestuff then colors the soln. blue. Of commercial methylene blue, dissolve 0.15 g. in 100 cc. of water. To 50 cc. of this soln. add 10 cc. of 0.1  $N$   $KI$  soln. dropwise while shaking. Add sufficient water to get a clear soln. above the tetra-iodide ppt. Titrate with thiosulfate till the soln. turns blue in transmitted light. Multiply the net cc. of 0.1  $N$   $KI$  soln. by 12.46 to get the % of hydrated methylene blue or by 10.66 to get the % of anhydride. W. T. H.

**Determination of the oxygen content of commercial oxygen.** B. NEUMANN AND W. SYEGER. *Chem.-Ztg.* 49, 585(1925).—The  $N_2$  content of commercial  $O_2$  is usually detd. by passing the gas over hot  $Cu$  to remove the  $O_2$  or by absorbing the  $O_2$  in alk. pyrogallol soln. The former method gives accurate results which correspond to the values obtained by absorbing  $O_2$  (1) in  $Cu$ ,  $(NH_4)_2CO_3$  and  $NH_4OH$ , (2) in  $Na_2S_2O_4$  and (3) with  $P$  after diln. with  $N_2$ . With pyrogallol, however, the values are found to be too high owing to the formation of some  $CO$  (0.4–3.8%) as a result of the action of  $O_2$  on the alk. pyrogallol soln. If the  $CO$  is removed from the residual gas, then correct values for  $N_2$  are obtained by means of alk. pyrogallol. W. T. H.

**The reliability of the quinhydrone electrode for the measurement of hydrogen-ion concentration in various solutions.** I. M. KOLTHOFF. *Z. physiol. Chem.* 144, 259–71 (1925).—In protein-free solns. the quinhydrone electrode gives excellent results if the  $pH$  is less than 9 and the soln. has a good buffer action. In solns. with insufficient buffer effect the limit is displaced to the acid side. In all cases good results are obtained at 18° if the  $pH$  is less than 8. Good results may be obtained in acid soln. by applying the equation of Billmann (*C. A.* 18, 3092) even if the buffer is deficient. Proteins interfere at alk. and sometimes even at neutral reaction, and the quinhydrone electrode shows a reaction too acid. The protein error is dependent on the nature and concn. of the protein and on the  $H$ -ion concn. The more alk. the soln. the greater is the disturbance and the less const. the result. The quinhydrone electrode is recommended for dairy investigations. A. W. DOX.

**The determination of acetaldehyde in the quantitative determination of lactic acid.** P. LEONE AND G. B. TAFURI. *Ann. chim. applicata* 15, 206–8(1925).—To avoid the difficulties and inaccuracies of the usual methods such as those of Partheil (*Z. Nahr. Genussm.* 5, 1049(1902)), Paris (*Staz. sper. agrar. ital.* 40, 689(1907)) and Ripper (cf. Clausen, *C. A.* 16, 2342), a method is described which is simpler and much more accurate when only a trace of lactic acid or of  $AcH$  is present and has the further superiority of using only stable solns. Advantage is taken of the fact that phenolphthalein is insensitive to  $NH_4OH$  whereas methyl orange is affected even by traces. **Procedure.**—Distill the lactic acid soln. with 50–100 cc. of 50%  $H_2SO_4$  maintaining the temp. at 140–50°. Collect the distillate in  $NH_4OH.HCl$ , the  $NH_4OH$  of which has been set free by addn. of  $NaOH$  to exact neutrality to phenolphthalein. During the distn. pass a slow current of air through the system. The  $AcH$  distd. forms an oxime with the  $NH_4OH$ . Titrate the excess  $NH_4OH$  with  $H_2SO_4$  using methyl orange, and calc. the  $AcH$  or the lactic acid from the difference between this and the original amt. To det. the latter neutralize 25 cc. of the  $NH_4OH.HCl$  soln. with  $NaOH$  (phenolphthalein) and then add a few drops of methyl orange and titrate with  $H_2SO_4$  the  $NH_4OH$  which is set free by the  $NaOH$ . Excellent results were obtained in the detn. of lactic acid extd. from muscle by the method of Meyerhof (*Arch. ges. Physiol.* (Pfluger's) 204, 301(1924)). C. C. DAVIS.

**The analysis of gaseous hydrocarbons, particularly olefins.** H. TROPSCH AND E. DITTRICH. *Brennstoff-Chem.* 6, 169–77(1925).—Fractional condensation at liquid-air temps was applied in the analysis of complex mixts of paraffins and olefins. Gases other than hydrocarbons are first detd. ( $CO_2$  by absorption in  $KOH$ ,  $O_2$  with alk. pyrogallol,  $CO$  with ammoniacal  $CuCl_2$  and  $H_2$  by selective combustion over  $CuO$  heated to 240°, at which temp. it is shown the higher hydrocarbons are not affected) and the residual hydrocarbons are then condensed by liquid air in an app. built by Ströhlein Co. Düsseldorf. Condensation and fractionation are carried out in 4 U-tubes cooled to suitable temps. by liquid air and also by  $Al$  blocks cooled by this medium. The fractionation is carried out under high vacuum maintained by a Töpler pump. A Gaede pump is also used for circulation of gases. The fractions obtained are:  $B$  (methane),  $C_1$  (ethane, propane, ethylene and propylene),  $C_2$  (propane, butane, pro-

pylene and butylene), *D* (olefins and paraffins of higher mol. wt.) From the individual fractions ethylene homologs are absorbed by 87%  $H_2SO_4$  and ethylene itself is absorbed by a mixt. of solns *a* and *b* in proportions 0.25-1.875, *a* being 87%  $H_2SO_4$  satd. with  $NiSO_4$ , and *b* being 87%  $H_2SO_4$  contg. 0.6%  $Ag_2SO_4$ . The amt. of carbon corresponding to each vol. absorbed is detd. by oxidation of the acid soln. with excess  $KIO_3$  and back-titration of the excess with  $Na_2S_2O_3$ . Paraffin hydrocarbons are detd. by combustion in small quartz tubes contg. heated  $CuO$ . Boiling curves of the hydrocarbons are given with numerous tables of analytical data for pure gases. Specimen analyses of (1) an oil gas, (2) a Synthol gas and (3) a gas from the Bergius hydrogenation process are given.

J. D. DAVIS

#### Separation of aliphatic amines from $NH_3$ (LEONE) 6.

Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists. 2nd ed. revised to July 1924. Washington, D. C.: Assoc. Official Agr. Chemists. Reviewed in *Cereal Chemistry* 2, 264(1925).

### 8—MINERALOGICAL AND GEOLOGICAL CHEMISTRY

EDGAR T. WHERRY

**Metasomatism.** WALDEMAR LINDGREN. *Bull. Geol. Soc. Am.* 36, 247-61(1925).—Presidential address. Metasomatism is defined as "an essentially simultaneous, mol. process of soln. and deposition by which, in the presence of a fluid phase, one mineral is changed to another of differing chem. compn." Special emphasis is placed on gel-metasomatism, or replacement of crystalloids by gels.

W. F. HUNT

Note on the elasticity of some minerals and its measurement. ALBERT JOHANNSEN AND T. C. PHENISTER. *J. Geology* 33, 268-71(1925).—The method employed consisted in dropping a hardened steel ball (wt. 7.2 grains) a standard height (200 mm.) on a specimen and measuring the height of the rebound (Gaston method). Fluorite, pyrite, quartz and garnet were found to be more elastic than steel (92). Some of the values obtained were: garnet 97; quartz 95.5 (prism face), 93.5 (pyramid face); pyrite 95, fluorite 93, labradorite 90; calcite 73.5; selenite 32.5.

W. F. HUNT

A note on the microscopic relations of sulfides and silica in blast-furnace and converter linings. T. C. PHENISTER. *J. Geology* 33, 278-85(1925).—A study of corroded linings, to det. means for differentiating sulfides formed by anhydrous melts from those produced by hydrothermal agencies. In the case of Pb-furnace linings, the structure resembles hydrothermal replacements, in that replacement has proceeded along the contacts between the silica grains. In the Cu-converter lining, veinlets occur as fissure fillings; this is distinct from the hydrothermal type of replacement.

W. F. H.

A notice of the occurrence of native arsenic in Cornwall; of bismuthinite at Shap, Westmorland; and of smaltite and nicothite at Conistone, Lancashire. ARTHUR RUSSELL. Chemical analysis. H. F. HARWOOD. *Mineralog. Mag.* 20, 299-304(1925).—Arsenic has been recently discovered in 2 localities in Cornwall. One occurrence, at Burraton Combe quarry, in joints in dolerite, contains: As 94.80, Sb. 5.15, Fe 0.15, S 0.11, insol 0.10%. The second is at Tolgus mine, Redruth, in slate. Bismuthinite occurs as long, fibrous or foliated blade-like aggregates, tarnishing yellowish or bluish on exposure. Smaltite and nicothite are intimately associated; the former in simple cubes with curved faces, up to 9 mm. along the edge.

W. F. HUNT

Polymorphic transformations of silica. LOUIS LONGCHAMON. *Compt. rend.* 180, 1855-8(1925).—The work of Feuner (*C. A.* 7, 579, 3945) is confirmed in general. The transformations into each other of quartz, tridymite and cristobalite are studied at temps. between 870° and 1470°. The pure cristobalite and tridymite, obtained in their zone of stability, gave the following constants: mean  $n_s$  1.487 and 1.477, and  $d_s$  2.347 and 2.266, resp.

L. W. RIGGS

The force of crystallization of calcite. E. P. ROTHROCK. *J. Geology* 33, 80-3(1925).—Geological evidence is submitted indicating a great force was exerted when calcite crystd. in the Nussbaum formation, Okla., sufficient to move considerable masses of rock material and also to split grains of quartz. As the tensile strength of quartz is 18,000-23,000 lbs. per sq. in., some idea may be obtained of the magnitude of the force.

W. P. HUNT

The optical character of albite. H. FISCHER. *Z. Krist.* 61, 226-49(1925).—Contains a bibliography and some analyses.

L. S. RAMSDALL

Potash-oligoclase from Mt. Erebus, Antarctic and anorthoclase from Mt. Kenya, East Africa. E D MOUNTAIN *Mineralog Mag* 20, 331-45(1925).—Two types of K-oligoclase were noted, differing in habit and color. Extinction on (001)  $3.4-2.6^\circ$ ; on (010)  $4.7-2.6^\circ$   $2V = 62^\circ$ .  $\alpha$  1.536,  $\beta$  1.539,  $\gamma$  1.541, compn:  $\text{SiO}_2$  62.79; 62.49,  $\text{Al}_2\text{O}_3$  22.12-21.86,  $\text{Fe}_2\text{O}_3$  0.36-0.30,  $\text{FeO}$  0.41-1.31,  $\text{CaO}$  3.76-3.74,  $\text{MgO}$  0-0.16,  $\text{Na}_2\text{O}$  7.35-7.20,  $\text{K}_2\text{O}$  2.98-3.26,  $\text{H}_2\text{O}$  0.26-0.04%; Or  $\text{Ab}:\text{An} \approx 18.64:18-19.64$  17. The anorthoclase from Mt. Kenya has the properties Extinction on (001)  $2.9^\circ$ , on (010)  $7.8$ ,  $\alpha$  1.526,  $\beta$  1.530,  $\gamma$  1.532;  $2V = 51^\circ$ ; compn:  $\text{SiO}_2$  64.33,  $\text{Al}_2\text{O}_3$  20.94,  $\text{Fe}_2\text{O}_3$  0.20,  $\text{FeO}$  0.58,  $\text{CaO}$  2.01,  $\text{Na}_2\text{O}$  7.22,  $\text{K}_2\text{O}$  4.71,  $\text{H}_2\text{O}$  0.37%; Or  $\text{Ab}:\text{An} \approx 27-63$  10. W. F. HUNT

Afwillite, a new hydrous calcium silicate from Dutoitspan mine, Kimberley, South Africa. JOHN PARRY AND F. E. WRIGHT *Mineralog Mag* 20, 277-86(1925).—The clear and colorless mineral was found in a dolerite inclusion in the kimberlite associated with apophyllite, calcite and natrolite. Analyses indicate the formula to be  $3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$ . The  $\text{H}_2\text{O}$  (15.81%) is driven off above  $115^\circ$  and is thus water of constitution. The filtrate from an aq. suspension of the powder material turns litmus paper blue and phenolphthalein pink. The mineral is inferred to contain 75.84%  $\text{H}_2\text{CaSiO}_4$  and 23.10%  $\text{Ca}(\text{OH})_2$  in chem. combination. Crystal system, monoclinic, elongated along  $b$  axis.  $a:b:c = 2.097:1.2381$ ;  $\beta = 98^\circ 26'$ . Perfect basal cleavage; hardness = 4, sp. gr. = 2.63.  $b = 6$ ,  $c = 10$ ,  $\alpha = +30.6^\circ$ , optic plane  $\perp$  elongation. Optically  $+$  with  $2V_D \approx 54^\circ 40'$ .  $\sigma = 1.6169$ ,  $\beta = 1.6204$ ,  $\gamma = 1.6336$ . The mineral was named after its discoverer, A. F. Williams. W. F. HUNT

Spherulites of reaumurite with helicoidal winding. P. GAUBERT *Compt. rend.* 180, 1853-5(1925).—A spherulite 8 cm in diameter, found at the bottom of a crucible for melting glass, was proved by its phys. properties to be reaumurite and not wollastonite; it showed the rare helicoidal structure. These 2 minerals are considered distinct, in opposition to Bowen (C. A. 16, 2652). L. W. RIGGS

An analysis of alvite. SARDES BEDR-CHAN, *Z. anorg. allgem. Chem.* 144, 304-5 (1923).—An av. of 2 analyses gives,  $\text{SiO}_2$  25.65 ( $\text{TiO}_2$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{Ta}_2\text{O}_5$ ) 0.63,  $\text{CaO}$  2.08,  $\text{MgO}$  1.11, rare earth oxides 2.76,  $\text{Fe}_2\text{O}_3$  7.57 ( $\text{Zr}$ ,  $\text{Hf}$ )  $\text{O}_2$  46.58,  $(\text{Al}_2\text{O}_3, \text{BeO})$  4.55,  $\text{H}_2\text{O}$  6.30, sum 97.23%. Single analyses showed the rare earths to contain 2.05%  $\text{ThO}_2$  and 0.78%  $(\text{Ce}, \text{Y})_2\text{O}_3$ ;  $\text{ZrO}_2$  41.92 and  $\text{HfO}_2$  4.66. The methods of analysis are outlined. E. F. H.

The chemical classification of the mica group. I. The acid micas. A. F. HALLIMOND *Mineralog. Mag.* 20, 305-18(1925).—Adoption of the principle that  $\text{R}_2\text{O}_3$  can be replaced by  $\text{RO}$  results in simplification of the formulas. The muscovites can be represented as mixtures of  $x[\text{K}_2\text{O} \cdot 3\text{R}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 2\text{H}_2\text{O}]$  (muscovite) and  $y[\text{K}_2\text{O} \cdot \text{RO} \cdot 2\text{R}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 2\text{H}_2\text{O}]$  (phengite). Chrome micas and paragonite resemble muscovite, while the analyses of damourite and sericite contain also analyses of minerals of "hydromicas" and some in which substitution of alumina by alkalies has occurred. Lepidolite is  $\text{K}_2\text{O} \cdot \text{Li}_2\text{O} \cdot 2\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 2\text{H}_2\text{O}$  with a considerable part of the  $(\text{OH})$  replaced by  $\text{F}$ . Cryophyllite is a mixture of  $\text{K}_2\text{O} \cdot \text{Li}_2\text{O} \cdot 2\text{R}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 2\text{H}_2\text{O}$  with  $\text{K}_2\text{O} \cdot \text{Li}_2\text{O} \cdot \text{RO} \cdot \text{R}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ . It is related to lepidolite in the same way as phengite to muscovite. Another mol.  $\text{R}_2\text{O}_3$  replaced by  $\text{Li}_2\text{O}$  yields  $\text{K}_2\text{O} \cdot 2\text{Li}_2\text{O} \cdot \text{R}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ , polyolithionite. Zinnwaldite could be regarded as mixts. of lepidolite with a Li-biotite (protolithionite) having the formula  $\text{K}_2\text{O} \cdot 2\text{Al}_2\text{O}_3 \cdot 3\text{RO} \cdot \text{Li}_2\text{O} \cdot 6\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ . Graphical formulas also are given. Cf. Winchell, C. A. 19, 2007. W. F. HUNT

A white chlorite from Madagascar. J. ORCEL, *Compt. rend.* 180, 1672-4(1925).—This mineral was found in the province of Ambatofinandrahana in homogeneous crystals with  $n_x$  1.5904,  $n_y$  1.5754 (calcd.),  $n_z$  1.5749; sp. gr. = 2.735. Analysis gave:  $\text{SiO}_2$  30.31,  $\text{Al}_2\text{O}_3$  21.72,  $\text{FeO}$  0.56,  $\text{MgO}$  34.63,  $\text{H}_2\text{O} + 13.30$ , sum 100.52%; formula  $7\text{SiO}_2 \cdot 3\text{Al}_2\text{O}_3 \cdot 12\text{MgO} \cdot 10\text{H}_2\text{O}$ . This mineral corresponds closely with leuchtenbergite and rumpite, and almost exactly with a mixt. consisting of 40% antigorite with 60% of amesite. L. W. RIGGS

The phosphate pegmatite of Hagendorf, Bavaria. New observations. F. MÜLLER-HAUER, *Z. Krist.* 61, 318-35(1925); cf. C. A. 15, 1001.—A survey of the geographical and geological character and discussion of the paragenesis of the minerals of this pegmatite. New minerals for this locality are triploidite, apatite, a white orthorhombic Mg phosphate (not identified), and 3 new monoclinic hydrated phosphates of Fe, Mn and Mg: *lehnerite*  $(\text{Fe}, \text{Mn}, \text{Mg})_2(\text{PO}_4)_2(\text{OH}) \cdot 5\text{H}_2\text{O}$ ; *wentzschite*  $(\text{Mn}, \text{Fe}, \text{Mg})_2(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$ ; and *baldaufite*  $(\text{Fe}, \text{Mn}, \text{Ca}, \text{Mg})_2(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ ; for which analyses, optical and crystallographic data are given. L. S. RAMSDELL

Tyuyamunite from the Tyuya-Myun radium mine in Fergana. P. N. CHIRVINSKI, *Mineralog. Mag.* 20, 287-95(1925).—Tyuyamunite,  $\text{CaO} \cdot 2\text{UO}_2 \cdot \text{V}_2\text{O}_5 \cdot m\text{H}_2\text{O}$ ,

is related to carnotite, differing in degree of hydration and in containing CaO in place of  $K_2O$ . The ore forms metasomatic veins and caverns in limestone, which around the ore is dolomitized. The State Expedition (1922) estimated 5000 tons of ore in sight = 60 tons of U and 15 to 20 g of Ra. Other mineralized veins have since been discovered. A new mineral, *kolouratite*, a vanadate of Na, has been found in the same region and seems to be widespread. Recently acquired material of tyuyamunite indicates orthorhombic crystals with (001), (010) and (100) cleavage; pleochroism, weak; mean  $n > 1.73$ ,  $\gamma - \beta = 0.024$ , dispersion  $p < v$ ; optical sign —, but + elongation; axial plane is (010) and  $Bx \perp (001)$ . The ore deposit is the result of post-volcanic hydrothermal action. Only secondary minerals in the upper zone have been found. Nothing is known of the primary minerals at depths. W. F. HUNT

The Olivenza meteorite (Spain). FERNANDEZ NAVARRO. *Compt. rend.* 180, 1674-6 (1925).—The fall occurred at 8 A.M., June 19, 1925; total wt. 140 kg. Analysis by Raoult gave.  $SiO_2$  40.73,  $Al_2O_3$  2.30,  $FeO$  20.74,  $MgO$  25.16,  $CaO$  2.09,  $Na_2O$  0.92,  $K_2O$  0.33,  $P_2O_5$  0.19,  $MnO$  0.15,  $Cr_2O_3$  0.14 (S 2.19, Fe 3.82), Fe 0.77, Ni 0.41, Co 0.02, undetd. 0.04, sum 100.00%; sp. gr. 3.453 to 3.456. The predominant mineral is olivine. L. W. RIGGS

The meteorites of Phu Hong (1887) and Tuan Tue (1921), Cochín China. A. LACROIX. *Compt. rend.* 180, 1977-80 (1925).—Analyses by Raoult of the Phu Hong and Tuan Tue meteorites gave, resp.: Fe 13.68, 9.93, Ni 1.21, 0.78, Co 0.02, 0.02, S 1.65, 2.24,  $SiO_2$  36.28, 40.35,  $Al_2O_3$  3.28, 2.97,  $FeO$  11.88, 14.93,  $MnO$  0.13, 0.21,  $MgO$  23.23, 25.19,  $CaO$  2.21, 1.99,  $Na_2O$  0.71, 0.67,  $K_2O$  0.21, 0.21,  $P_2O_5$  0.21, 0.29,  $Cr_2O_3$  0.11, 0.14, loss at  $105^\circ$  0.06, 0.06, sum 99.97, 99.98%. These figures and the results of microscopic study indicate that the Phu Hong stone should be classified among the chondrites with olivine and bronzite, and the Tuan Tue meteorite among the chondrites with olivine and hypersthene. The presence of the rare mineral merrillite was noted. L. W. RIGGS

Geology and coal resources of the Axial and Monument Butte quadrangles, Moffat County, Colorado. E. T. HANCOCK. U. S. Geol. Survey, *Bull.* 757, 132 pp. (1925).—Chem. analyses of 26 samples from this field and 9 samples from neighboring fields showed that the coal ranges from sub-bituminous to bituminous in variety. The estd. quantity of coal in these quadrangles runs into billions of tons. L. W. RIGGS

Reconnaissance of the Point Barrow region, Alaska. SIDNEY PAIGE, W. T. FORAN and JAMES GILLULY. U. S. Geol. Survey, *Bull.* 772, 32 pp. (1925).—The object of this exploration was to det. the petroleum prospects of this region. The geographical and geological features of the region are described, also 2 oil seepages at Cape Simpson. A sample of the weathered oil showed a small proportion of the lighter hydrocarbons, the more volatile constituents probably had been lost by evapn., and a large proportion of naphthalene hydrocarbons and lubricating fractions. The evidence thus far obtained warrants a continuation of the exploration. Coal of sub-bituminous to bituminous varieties was found in workable beds covering an area of at least 1000 sq. mi. L. W. RIGGS

Tourmalinization in the Dartmoor granite. A. BRAMMALL and A. F. HARWOOD. *Mineralog. Mag.* 20, 319-30 (1925).—The usual types of the Dartmoor granite can be referred to 4 intrusions ranging from basic to acid with corresponding increase in tourmaline content. In the latest stage of intrusion the concn. of volatile constituents was such that the intrusive bodies were pneumatolyzed before crystn. was complete. During the closing phase fissures were opened and filled with quartz-tourmaline rock, vein quartz, or ore bodies carrying hematite or cassiterite. The last phase was marked by local tourmalinization of granite in place. The Ti content of biotite and ilmenite forms titanite and rutile when tourmalinization takes place at magma temp., and anatase, brookite or rutile under conditions of post-solidification pneumatolysis. W. F. H.

Two modes of existence of hydrocarbons in bituminous shales. JACQUES DE LAPPARENT. *Compt. rend.* 180, 1676-8 (1925).—Bituminous shales yield but a small part of their hydrocarbons to the usual solvents as compared to their yield upon distn. A portion of the hydrocarbon is in the form of minute liquid drops the removal of which by solvents depends largely upon the fineness with which the rock is pulverized. In shales of the boghead variety, hydrocarbons are considered as gels pptd. in the colloidal state and later becoming cryst. L. W. RIGGS

Relation of hydrocarbons and of carbonates in flints and cherts. JACQUES DE LAPPARENT. *Compt. rend.* 180, 1858-9 (1925).—In certain limestones of Alsace and of Czecho-Slovakia are found flint or chert portions from which carbonate crystals have disappeared and their places have been partly or wholly occupied by liquid hydrocarbons. L. W. RIGGS

The average composition of the earth's crust in Finland. J. J. SEDERHOLM *Bull. Comm. Geol. Finlande* No. 70, 20 pp (1925).—The av. of 101 analyses of Finnish rocks weighted according to the areal extent of the several types represented, gave:  $\text{SiO}_2$  67.45,  $\text{TiO}_2$  0.41,  $\text{Al}_2\text{O}_3$  14.63,  $\text{Fe}_2\text{O}_3$  1.27,  $\text{FeO}$  3.28,  $\text{MnO}$  0.01,  $\text{MgO}$  1.69,  $\text{CaO}$  3.39,  $\text{Na}_2\text{O}$  3.06,  $\text{K}_2\text{O}$  3.55,  $\text{P}_2\text{O}_5$  0.11,  $\text{H}_2\text{O}$  0.79,  $\text{CO}_2$  0.12, other minor constituents, 0.01%. The rocks included in this av. occupy 68% of the pre-war area of Finland; 11% being unsurveyed at the time of calcul., and migmatites covering 21%. S's av. differs from those of other authorities, and he attributes this to the facts that (1) others did not consider the areas of the rock types averaged, and (2) there is an undue preponderance of analyses of rare and limited rock types. E. F. H.

The analysis of gases obtained from volcanoes and from rocks. F. S. SHEPHERD *J. Geology* 33 (supplement to No. 3), 299-370 (1925).—The article describes in great detail the methods used in collecting and analyzing the gases and other volatile products. It was found that while C, H and O were nearly constant in a series of runs on the same material, the halogens and S varied considerably, depending upon the temp. at which the material was collected. The vol. % at 1200° and 760 mm. pressure were as follows:  $\text{CO}_2$  11.76-11.17;  $\text{CO}$  0.15-0.05;  $\text{H}_2$  0.38-0.46;  $\text{N}_2$  0.28-1.31; A tr.,  $\text{SO}_2$  0.00-0.01;  $\text{S}_2$  1.66-1.67;  $\text{Cl}_2$  1.33-1.03,  $\text{F}_2$  3.61-6.20,  $\text{H}_2\text{O}$  80.83-78.10. W. F. HUNT

Geochemical distribution laws of the elements (GOLDSCHMIDT, *et al.*) 2. Dispersoids of the mineral world and of slags (LORENZ, EITEL) 2.

## 9—METALLURGY AND METALLOGRAPHY

D. J. DEMOREST, ROBERT S. WILLIAMS

The production of cadmium. N. P. BUDGEN. *Ind. Chemist* 1, 293-7 (1925).—A review. E. H.

Cadmium in 1923-1924. C. E. SIEBENTHAL AND A. STOLL. U. S. Geol. Survey, *Mineral Resources of U. S. 1924*, Part I, 7-11 (preprint No. 2, published 1925). E. H.

Quicksilver in 1924. C. P. ROSS. U. S. Geol. Survey, *Mineral Resources of U. S. 1924*, Part I, 13-9 (preprint No. 3, published July 30, 1925). E. H.

Tin in 1924. B. L. JOHNSON. U. S. Geol. Survey, *Mineral Resources of U. S. 1924*, Part I, 31-3 (preprint No. 5, published Aug. 7, 1925). E. H.

Application of the flotation process to gold ores. B. H. MOORE AND A. S. WINTER. *Chem. Eng. Mining Rev.* 17, 353-7 (1925).—Flotation of colloidal slime with the pyrite is prevented by agitation by an impeller and by subaeration. Flotation is then more effective and more rapid. The chief cost of flotation is in the fine grinding. "Sweet" roasting is essential for low cyanide consumption. Exptl. results on Kalgurli ore are tabulated and tests on several other ores are outlined. W. H. BOYNTON

Differential flotation of copper and iron sulfides. H. E. KEYES. *Eng. Mining J.-Press* 120, 135-6 (1925).—A report of preliminary work on microscopic examn. of ores to det. the degree of association of the minerals. Tests show the importance of cyanide as a reagent for dropping pyrite. Reagents and methods are studied. The ore is ground to a pulp contg. 30-80% water and treated with cyanide and an alkali salt. Heating the ore pulp before floating is advantageous. Cyanides may play an important role in solving the metallurgical problems of the Southwest. W. H. B.

The development of a process for the treatment of weathered slimes at Broken Hill. R. D. NEVETT. *Chem. Eng. Mining Rev.* 17, 343-8 (1925).—Exptl. work on the treatment of weathered slimes extending over a period of 6 years is outlined and the treatment developed for commercial-scale work is described. The Leggo straight-line 4-hearth furnace is fired with producer gas under reducing atm. conditions. The hearths are superimposed and work in parallel, and each of the ten columns is fitted with an arm and teeth for each hearth. The four zones are the drying, heating and reducing zones and the gas-combustion chamber. The gas passes in a direction opposite to that of the ore. Controlling factors of the process are: (1) the addn. of a reducing agent; (2) the temp.; (3) a reducing atm., which is maintained by keeping a plus pressure in the furnace and by allowing a little of the gas to pass through the furnace unburnt; and (4) quenching the slime in water before it comes in contact with air. Charcoal is the reducing agent; it is used in the proportion of 13 lbs. (5.9 kg.) per ton (907 kg.) of slimes. W. H. BOYNTON

Some observations on the industrial production of zinc. GAETANO CASTELLI.

*Rass min mel chim* 62, 77-81(1925)—A review and discussion of modern practice and of the relative merits of the C reduction and electrolytic processes for producing Zn from various ores. C. C. DAVIS

Principles of metallurgy of ferrous metals for mechanical engineers. IV. Heat treatment. LEON CAMMEN *Mech. Eng* 47, 638-42(1925); cf. C. A. 19, 2467.

E. H.

Remarks on the blast-furnace process. J. J. VAN LAAR. *Chem. Weekblad* 22, 367-70(1925), cf. Korevaar, C. A. 19, 2445—In calcg. the heat balance of the blast furnace Korevaar disregards entirely the reduction of the ore. A sep. consideration of combustion and reduction is thermodynamically not permissible. K.'s formula does not express the fact that the fuel consumption decreases with the rising temp of the blast; it even seems to postulate the opposite conclusion. K.'s calcn furthermore anticipates that the entire combustion heat is lost by radiation. L. gives a formula of his own by combining both the reduction and combustion process;  $Fe_2O_3 + 3C + 3CO = 2Fe + 6CO$  and by assuming an av temp of 1600° throughout the entire furnace. At this temp the equil is practically entirely on the CO side. The calcn. shows that a rise of the furnace temp requires a considerable rise of the air temp. even if the quantity of coal as compared with the ore be  $\infty$ . A formula for the equil  $C + CO_2 = 2CO$  is developed and the error of applying Nernst's heat theorem in such calcns is pointed out, in view of the fact that the theorem is valid only near zero abs. MARY JACOBSEN

Reply to J. J. van Laar. A. KOREVAAR. *Chem. Weekblad* 22, 370-1(1925).—Van Laar's views (preceding abstract) are incompatible with technical considerations. It is not permissible to assume a uniform temp. of 1600° throughout the entire furnace. The chem. reactions and their heats are different in the different zones. Moreover L.'s interpretation of K.'s formula is incorrect. MARY JACOBSEN

The investigation of metals by means of X-rays. TH NEEFF. *Z. tech. Physik* 6, 208-16, 250-8(1925)—The different factors which play an important part in the detn. of errors in the investigations of metals with X-rays are discussed, e. g., errors due to photography, and the effects of scattered radiation. J. H. PERRY

Scratch and Brinell hardness of severely cold-rolled metals. M. F. FOOLER AND E. J. QUINN. *Trans. Am. Inst. Min. Met. Eng* 1925 (advance copy) 6 pp.—Both the Brinell and scratch tests for the hardness of Cu and Fe showed figures increasing to a const. value on continued cold rolling of the metals. A Cu bar, 1 in. thick and having a Brinell no. 33.4, increased in hardness to a value 116 when rolled to a thickness of 0.027 in. Below this thickness the figure for hardness decreased slightly. The increase in hardness as indicated by the scratch test is not of the same magnitude as that shown by the Brinell method; this may be accounted for by the lack of sharpness of the Brinell impressions on the hardened metal. B. C. A.

Heat and atomic motion. G. MORESSÉE. *Rev. universelle mines* [7] 6, 66-88 (1925).—Laws are derived for the atomic motion in metals, including the influence of the speed of rotation, radius of gyration and frequency of rotation of the atoms and the relation of these factors to temp. The treatment is almost wholly mathematical, but certain general laws are derived, e. g., that (1) the characteristic frequency is proportional to the sq. root of the m. p., to the cube root of the d. and is inversely proportional to the  $1/4$  power of the mol. wt. of the metal; (2) when the radius of at. gyration reaches  $1/11$  of the radius of the sphere of mol. action, the metal becomes liquid and (3) the radius of gyration of a metal is proportional to the sq. root of the temp. The original paper must be consulted for further details. C. C. DAVIS

The strength of materials as a resultant of atomic forces. G. MORESSÉE. *Rev. universelle mines* [7] 6, 89-93(1925); cf. preceding abstr.—The load at the elastic limit of metals and its variation with the temp are derived mathematically. The load which a metal can bear at the elastic limit is proportional to the m. p. (based on the abs. temp.) and to the d., and is inversely proportional to the mol. wt. (twice the atomic wt.). The equation  $F = [(18.07T_1/3)/P]^{1/2} [1 - \sqrt{T/\sqrt{T_1}}]$ , where  $F$  is the load in kg. per cm<sup>2</sup> at the elastic limit,  $T_1$  is the m. p. (abs.),  $\Delta$  is the d.,  $P$  is the mol. wt. and  $T$  is the abs. temp. of the expt., gives the load as a function of the m. p., the d. and the mol. wt. From this, calcns. show that the loads at the elastic limit of Fe, Al, Cu and Pb are 368, 354, 312 and 90 kg. per cm<sup>2</sup> at ordinary temps. From this formula may be derived the expression  $R' = R[(\sqrt{T_1} - \sqrt{T})/(\sqrt{T_1} - \sqrt{T})]$ , where  $R$  is the strength at the elastic limit of an alloy at temp.  $T$  and  $R'$  is its strength at another temp.  $T'$ , which gives a correction factor to be applied to alloys for changes in temp. Thus calcns. show that for a semi-hard steel with breaking strength of 6500 kg. per cm<sup>2</sup> and elastic load of 4000 kg. per cm<sup>2</sup> at 15° and m. p. of 1300° the values of  $R'$  decrease as follows with increase

in temp. 288°, 4000; 473°, 3160, 673°, 2440, 873°, 1800, 1073°, 1240; 1273°, 480; 1473°, 200; 1573°, 0. The law should be of technical application in the hot working of metals, e. g., forging and rolling. C. C. DAVIS

Fatigue failure of brass tubes; nature of fatigue. W. E. W. MILLINGTON AND F. C. THOMPSON. *J. Inst. Metals* 31, 81-103; Disc 103-20(1924); *Science Abstracts* 27B, 461-2.—The failure took place in a large water-heater of the tubular type; the tubes were of solid-drawn 70/30 brass, annealed at the ends, and after 2 weeks 2 tubes broke on a plane at right angles to their length and well within the annealed portion. There was no evidence of corrosion, the fracture was not of the season-cracking type; Hg cracking tests showed no signs of undue internal stress, and the analysis was satisfactory. The material was apparently quite ductile, and the surface of the fracture was that peculiar to fatigue failure. Micro-exam. near the fracture showed the material to be normal except for the presence of many straight lines in several of the crystals, which had the characteristics of Newman bands. It was concluded that the failure must be due to fatigue caused by the vibration of the tubes, and after replacing them and providing brass spacing plates to stiffen the tubes against vibration, no further trouble was met within twelve months' working. It is suggested that the straight lines found in the specimens are the cause of embrittlement, which leads to failure instead of being a mere indication by which fatigue may be diagnosed. Further exam. showed that the markings are bars instead of bands, and the orientation of these bars is quite different from that of the crystal in which they occur. A theory of the formation of these bars is suggested and illustrated by means of models built up with balls. H. G.

The properties and testing of magnetic materials. Permanent magnet steels. T. SPOONER. *Elec. J.* 22, 394-401(1925).—Essential requirements for magnets include a high coercive force, high residual induction, and magnetic permanency. Cast Fe, plain C steels and various alloys are used. Mn, Ti, Cu, S and P are to be avoided, while W, Cr, C and Co are advantageous constituents. W steels maintain their magnetism well as do certain Co alloys. A Co-Cr alloy contg. C 1, Cr 9-14, and Co 1-18% is self-hardening and possesses magnetic properties but little inferior and at a lower cost than the best Japanese steels. Means of measuring the magnetism and a bibliography are included. A Cr steel contg. 6.23% Cr and 1.14% C is being widely used. W. H. BOYNTON

The practice and purpose of Perlit iron. H. J. YOUNG. *Metal Industry* (London) 27, 10-2(1925).—The Perlit process consists in casting low-Si Fe at a controlled temp into definitely heated molds. Authorities are quoted to show that Fe with small graphite particles in a pearlitic groundmass is most desirable. Perlit Fe is remarkably resistant to impact, and is superior in "size, shape and distribution of voids partly filled with graphite." Photomicrographs show graphite, phosphide, and lamellar pearlite, but no ferrite. The structure is claimed to be more uniform from center to edge than in ordinary castings. The compn. used would give white Fe if poured in ordinary cold sand molds. G. F. C.

Process of manufacture as affecting special steels. W. ERLENDER. *Stahl u. Eisen* 44, 1637-44(1925).—Special steels must (1) show consistently high performance, (2) be non-sensitive during heat treatment, (3) admit of flawless fabrication. To det. this in advance these tests are relied on: chem. analysis, microstructure, amount and distribution of inclusions, surface or interior defects. The microscope fails when the inclusions reach a certain minimum size; but these sub-microscopic inclusions greatly affect the quality of the steel. Nitrogen is not much absorbed; hydrogen, though largely dissolved, is made harmless by Al or Si additions. CO and CO<sub>2</sub> have slight soly. This leaves O<sub>2</sub> to be considered. This is harmful to the steel, especially in the combined form. The effect of the oxide depends on whether it is present in globules or films, whether of high or low melting point, whether of high or low sp. gr. (floatation). These oxides affect not only hot steel but also cold steel, cf. "woody fracture," etc. Endurance of steel in service is much lowered by their presence. The process of manuf. directly affects the amounts of oxygen. P and S are also harmful, but as they are kept low in the steels here considered it is not their amount but their tendency to cause segregation that harms. These spots are brittle and lower the endurance value. The harmful effect of P is increased by higher O<sub>2</sub> content. Considering how the various processes meet these demands, E. concludes that the open hearth is good for certain grades of special steels; the elec. furnace is good for most; but where the highest quality is demanded the crucible process is preëminent. The use of vacuum elec. furnace bids fair to give this process the lead. A. HUNGELMANN

Damascene steel. K. HARNECKER. *Stahl u. Eisen* 44, 1409-11(1924).—The basic idea is to obtain coarse primary hypereutectoid cementite and to break it up by

proper forging. Overheating must be avoided. The spheroidized cementite retains the general shape of the primary cementite pattern. Photomicrographs are given.

A. HUNGELMANN

Inner crystalline structure of ferrite and cementite in pearlite. N. T. BELAIEV. *Proc. Roy. Soc. (London)* 108A, 295-306 (1925). cf. C. A. 16, 2294.—From a microscopic study of pearlite under high power magnification (up to 4000X) B. was able to reveal the structure of the cementite and the ferrite lamellae. A cementite lamella shows a petal-like shape and curvature. The exposed edge has rectangular "steps" caused by a cleavage through a definite linear unit of about 250-300  $\mu$ . As a result of stresses during and after the formation of pearlite, the cementite lamellae become warped and twisted giving rise to steps in the cleavages. Every ferrite lamella (thickness 3 X that of a cementite lamella) is apparently composed of a conglomerate of small cubes, similarly but not uniformly oriented. The edge of the fundamental cube is about 250  $\mu$ . Isolated cubes of ferrite were found by B. in 1921 in the martensitic ground mass of Damascus blades. Their existence has also been confirmed by Lucas (C. A. 19, 1120). Eight photomicrographs are included.

H. S. VAN KLOOSTER

Plastic deformation of iron and the formation of Neumann lines. WALTER ROSEY-HAIN AND JEAN McMINN. *Proc. Roy. Soc. (London)* 108A, 231-9 (1925).—The authors have made a microscopical study of the manner in which variations in speed of compression affect the mechanism of deformation in plastic metals. Small rectangular prisms of annealed Armco Fe, Swedish wrought Fe and remelted electrolytic Fe were used. These materials behaved similarly. Slow deformation under the testing machine produced slip bands. Deformation by a blow of a weight of 50 lb. caused Neumann lines. These lines do not disappear on repolishing and are therefore due to lamellae running through the crystals. Slow deformation in a specimen previously deformed by a blow produced slip bands side by side with already existing Neumann lines. However, they cross these lines irregularly and do not suffer a uniform angular deviation as is the case when slip is produced in twinned Cu. For this reason R. and McM. do not consider Neumann lamellae to be identical with twinned layers. In many cases a thick black Neumann band branches out into diverging thin lines. In studying samples first slowly deformed and then directly subjected to a blow no trace of Neumann lines could be observed. A rest period of from one to four days after the application of slow stresses restores the material to the condition where impact produces Neumann lines. The authors conclude that the mechanism of deformation is the same for slow and sudden deformation. The difference resides in the manner of distribution of the slipping process. A number of photomicrographs accompany the paper.

H. S. V. K.

Method of developing Hartmann lines. PAUL OBERHOFFER AND MIA TOUSSAINT. *Stahl u. Eisen* 44, 1330-2 (1924).—On polished surfaces of soft steel relief lines appear on passing the elastic limit; or if scaled, the mill scale breaks along these lines. The present paper is a critical examn. of Fry's method of etching for these lines; time and cost are less if, instead of immersion only, an elec. current also is used. Dil. HCl with a little FeCl<sub>3</sub> and with a current of 0.2-0.3 amp. per sq. dm. of test piece gave the best results. The surface may be rubbed to observe the process of etching. Photographs are included.

A. HUNGELMANN

A new process for the manufacture of cast iron pipes. PAUL DOAT. *Rev. universelle mines* [7], 6, 306-12 (1925).—The new de Lavaud centrifugal process involves rapid cooling of the pipe, as a result of which the surface is hard. Micrographic examn. reveals a large amt. of cementite and some pearlite in the surface layer. Deeper in (below 1-2 mm.) cooling is slower and graphite is found. Subsequent thermal treatment overcomes this heterogeneity of structure and gives a uniform pearlite structure with small nodules of graphite. Phys. tests show that pipe made by the de Lavaud process is much harder and of much higher quality than that made in the ordinary way.

C. C. DAVIS

Black (graphitic) fracture in high-carbon steel. F. RAPATZ AND H. POLLACK. *Stahl u. Eisen* 44, 1509-14 (1924).—Black fracture occurs only when both pptn. of graphitic carbon (temper carbon) and its elongation by forging take place. Pptn. of the graphite is the more liable to occur the higher the temp. above the cementite line but not above the line of soln. of graphite. For 1.30 to 1.40% C steel this is 1000-1050°. After cooling from this temp., if the steel is held a long time at 700-800°, much graphite forms, and upon being elongated by forging, the steel shows the black fracture. Even if it is not forged a clear fracture is no indication of proper condition of the steel. 0.5 Cr prevents the graphite pptn. As expected higher Si promotes it.

A. H.

Effect of sulfur on structural steel. G. K. BURGESS, et al. *Proc. Am. Soc. Testing*

**Materials 24, 1, 185-205(1924)**—The material used in these tests was from 6 heats of basic open-hearth steel, S, in residual form, ranging from 0.03 to 0.08%, C from 0.19 to 0.25%, Mn from 0.41 to 0.48%, P from 0.012 to 0.015% and Si from 0.007 to 0.028%. All specimens were tested in tension, impact (Charpy), hardness (Brinell and scleroscope), bending and shear, both in the natural condition "as received" and in the annealed condition. In annealing, the material was heated to 870-900°, held for 1 hr. and cooled in the furnace. In normalizing it was heated to 870°, held 1 hr. and cooled in air, and in quenching it was heated to 900°, held 1 hr. and quenched in H<sub>2</sub>O at 21-23°. Tests were made at the Watertown Arsenal, Watertown, Mass., and at the U. S. Naval Engineering Expt. Station, Annapolis, Md. Curves are plotted showing the variation of the physical properties mentioned above with varying S content in the natural, annealed, normalized, and quenched condition. The av. C and Mn content are also plotted against av. S content of each heat. The joint committee has deferred to a later date any extended discussion of the results, and the drawing and publishing of any conclusions therefrom. H. STOERTZ

**Effect of sulfur on endurance properties of rivet steel.** G. K. BURGESS, *et al.*, *Proc. Am. Soc. Testing Materials* 24, 1, 90-107(1924).—Tests were made at the U. S. Naval Eng. Expt. Station. The steel investigated was in the form of rivet bar material. Av. C was 0.115% and Mn 0.442%. S varied from 0.0282 to 0.1793%, and P from 0.0055 to 0.0240%. Test machines were of the rotating cantilever type and high-speed alternating-torsion inertia type. Two types of heat treatment were used: (1) holding at 940° for 1/2 hr. and cooling in a furnace, (2) holding at 940° for 1/2 hr. and quenching in H<sub>2</sub>O at 21°. Detailed results of these tests are shown in tables and curves. In general the ratio of the endurance limit for 10<sup>7</sup> cycles, detd. with rotating cantilever, to the av. tensile strength is about 0.486 for annealed material and 0.515 for quenched material, while the ratio of endurance limit, detd. with alternating torsion, to the av. tensile strength is about 0.247 for annealed steel and 0.306 for quenched steel. Detn. of endurance limit by the "accelerated fatigue" method is more reliable than detn. the limit of proportionality in the stress-deflection graph. H. STOERTZ

**Metallographic investigation of effect of sulfur on rivet steel.** GEO. K. BURGESS, *et al.*, *Proc. Am. Soc. Testing Materials* 24, 1, 108-84(1924).—The material used was from 14 heats of rivet steel and is described in the first preliminary report. There are 3 parts to the investigation: (1) macroscopic, (2) non-metallic inclusions, (3) microscopic. (1) S prints give the best indication of macrostructure; a cross-section and longitudinal section of each specimen are shown in photographs. Samples of commercial rivet steel are included. In general the macrostructure, as shown by the color of the S prints, indicated S segregation, characterized by a light central core of varying shape surrounded by a layer of apparently much higher % S, and this in turn is in some cases surrounded by a layer with apparently little higher % S than the core. In several of the commercial samples this condition is reversed, the core appearing to have the higher % S. Chem. analyses from various sections of the specimens, however, show little or no segregation of S, showing that S prints do not always give a reliable indication of even the qual. distribution of S in a section of steel. (2) The sections examd. for non-metallic inclusions were longitudinal surfaces of Charpy impact specimens. Photomicrographs at a magnification of 100 are given. They show that inclusions other than sulfides constitute an important proportion of the total quantity of inclusions. With increase in S, the proportion of inclusions other than sulfides decreases. Two types of inclusions are prominent, the elongated manganese sulfide particles, and round inclusions occurring in streaks or irregular groups. Comstock's explanation of these as due to Al used as a deoxidant is not confirmed. Any direct effect of S on the physical properties of steel is probably due to the influence of manganese sulfide inclusions, but their effect is obscured by the effect of other inclusions, especially in low-S steel. (3) In studying microstructure, specimens were cut from each heat, all were placed in the same furnace, heated above the critical range, and cooled at different rates, one set being quenched in H<sub>2</sub>O, another in oil, a third cooled in air, a fourth cooled in the furnace, a fifth in iced brine, and others in air blast at different rates. They were then examd. at a magnification of 100; photomicrographs are shown. In the specimens quenched in H<sub>2</sub>O and iced brine, as S increases there is a general variation from a coarse network to a finer network and thence to a granular structure. This is more conspicuous in the oil-quenched specimens. In a set cooled in the air blast in 14 sec. the coarse network structure is found in the specimens of lowest S content, 0.028 to 0.035%. With higher S the granular structure predominates. The proportion of sorbite or sorbitic pearlite decreases and free ferrite increases with increase in S, in all types of heat treatment. Two specimens of low S content, 0.028 and 0.031%, and 2 specimens of high S content, 0.083 and 0.179%.

were examd. at magnifications of 1000 and 4000, and photomicrographs are shown for the various rates of cooling. The results obtained under these conditions confirm those obtained at lower magnifications, the amt. of free ferrite being greater with higher S. The dark areas at 100 diameters, which are complexes of ferrite and cementite, were studied to det. whether the difference in proportion of this carbide complex to free ferrite in low- and high S steels is due to difference in size of cementite particles, difference in degree of dispersion of cementite particles, or both. The results seem to indicate that differences in microstructure between low- and high-S steels are due rather to differences in distribution of the cementite particles, the tendency being toward agglomeration of these particles in high-S steels, this agglomeration being greatest at the boundaries of the carbide complexes. The sharp lines of demarcation between free ferrite and agglomerated cementite particles are found to be ferrite grain boundaries, and it is the variation in the total growth of these ferrite grains which causes the variation in the microstructure of these rivet steels with increase in residual S. In a set of specimens cooled at the same time through the critical range, the total growth of ferrite grains is greater the higher the % S. A study of this variation in microstructure in light of thermal changes that occur during rapid cooling of low C steel is made, and the conclusion reached that in rapidly cooled rivet steels there are 2 kinds of microstructure, the type in any region depending upon the presence or absence of nuclei of some kind in that region at the time of quenching. A region affected by nuclei consists of ferrite grains with adjacent layers of agglomerated cementite. A region unaffected by nuclei consists of a carbide complex of the same chem. compn. as that of the entire specimen. In the rivet steels prep'd. for the joint committee, the number of nuclei are approx. proportional to the % S. The theories of various investigators regarding the nature of these nuclei are presented, but no definite conclusions are drawn for the steels examd. There is some indication that the number of nuclei may be more nearly proportional to the total number of non-metallic inclusions rather than to the S content, but it is pointed out that this may be merely a coincidence. It is also possible that the microstructure depends more on a relatively large number of submicroscopic inclusions than the relatively small number of visible inclusions. Nuclei similar to those discussed exist in large numbers in heats of abnormal hypo-eutectoid steels that do not contain high S. A discussion is appended on the reliability of S prints as an indicator of the qual. distribution of S in a section of steel. The S print of a rail section is shown. H. STOERTE

"Peeling" in white-heart malleable. D. H. INGALL AND H. FIELD. *J. Iron and Steel Inst.* (advance proof) No. 9, 14 pp. (May, 1925); *Engineering* 119, 634-5.—Peeling is a common defect in European malleable iron, and does not greatly affect the mechanical properties, but interferes with good machining. Different samples of iron, 3.5 ir. by  $\frac{1}{2}$  in. square, were annealed in an exptl. furnace in different ways to det. the factors controlling this defect. The amount of peeling was tested by visual examn. of bars bent in a vise with a hammer. The exterior parts of bars which peeled were found to contain globules of oxide and to be sep'd. from the interior by more or less continuous layers of oxide. The interiors of the bars were ferrite, oxidized next to the peel, and contg. pearlite at the center. Chem. compn. did not seem to govern the peeling, except that peeling seemed most easily produced with higher Si, and with S between 0.2 and 0.4%. Low-temp. annealing reduced the tendency to peel, but did not give soft castings. High-temp. annealing suppressed the tendency to peel. The growth of peel progressed with time at 950°. The S content was lower in the peel than in the interior. Rapid heating was an important factor promoting peeling, and peeling commenced with the annealing effect. Tests under works conditions confirmed the results of lab. expts. The cause of peeling is tentatively explained as the result of oxidation at temps. above 900° or 940°, progressing faster than the rate of C supply by diffusion from the interior. G. F. COMSTOCK

The effect of grain upon the fatigue strength of steels. L. AITCHISON AND L. W. JONVSON. *J. Iron and Steel Inst.* (advance proof) No. 1, 26 pp. (May, 1925); *Engineering* 119, 585.—A large number of typical engineering parts are subject to fatigue stresses that are applied at various angles with the fibrous structure or "grain" of the metal. To investigate the effect of this angle on the endurance and other properties, slabs from large ingots, in which there was no "grain," and also specimens in different stages of forging down to 96% reduction, were tested in various directions. Mild steel, alloy steel, Armco iron, and wrought iron were used. The direction of the grain had a marked influence on the ductility and toughness, these values being much less in transverse specimens. The max. stress was not affected. The fatigue strength of lengthwise specimens was not over 17% greater than that of transverse specimens, the difference being almost negligible in most instances. Microstructures are illustrated and discussed.

Wrought iron gave erratic fatigue values. The fatigue fractures of the transverse specimens were stepped, the fracture showing a tendency to sep the fibers lengthwise at each step. This effect was specially coarse and noticeable in the wrought irons. The cause of the occasional slight inferiority of the transverse specimens, as compared with the lengthwise, in fatigue was probably the presence of a fine inter-fibrous sepn. at the point of max stress on the surface of some of the transverse specimens.

G. F. COMSTOCK

Heat treatment of cast iron. FRED GROTT'S *Trans Am Soc Steel Treating* 7, 735-42(1925).—Hard spots due to combined C can be removed by heating to 1750° F. Chilled Fe can be softened, then rehardened by heat treatment. White Fe can be quickly carburized by heating to 1750° F, then quenching and drawing. There is a certain application for hardening and drawing cast Fe. The addition of steel increases tensile strength.

W. A. MUDGE

Facts and principles concerning steel and heat treatment. H. B. KNOWLTON. *Trans. Am Soc Steel Treating* 7, 374-405, 743-73(1925).—Elementary articles selected primarily for their educational and informational character as distinguished from reports of investigation and research.

W. A. MUDGE

Carburizing and heat treatment of carburized objects. B. F. SHEPHERD. *Trans. Am. Soc. Steel Treating* 7, 774-89(1925).—Recommendations for carburization and heat treatment of carburized parts based on av practice in several mfg plants.

W. A. MUDGE

Heat treatment of high-speed steel dies. C. B. SWANDER. *Trans. Am. Soc. Steel Treating* 7, 727-34(1925).—Tightly sealed graphite crucibles with a small quantity of silica sand and charcoal in the bottom permit good hardening of high-speed steel dies and circular form tools, without scaling, blistering or distortion to any marked degree. Dimensional changes and necessary precautions are discussed.

W. A. M.

The manufacture and heat treatment of large forgings. A. O. SCHAEFFER. *Trans. Am Soc. Steel Treating* 7, 699-717(1925).—A detailed description of melting, pouring, hot top, ingot mold design, heating, forging and heat treatment.

W. A. M.

The structure of quenched carbon steels. B. D. ENLUND. *Jernkontorets Annaler* 77, 389(1922); *J. Iron and Steel Inst* (advance proof) No 3, 10 pp.(May, 1923).—The changes of elec. resistivity and sp. vol. with annealing temp. were investigated in low- and high-C steels. The resistance curves for all the steels showed breaks at 110° to 120° and 250° to 260°, indicating pptn of cementite. The first break was caused by the transformation of martensite into troostite, and the second by the splitting up of austenite into alpha iron and cementite. All C steels quenched in water in the ordinary way contain some austenite or gamma iron. The results were checked with specimens quenched at different temps and annealed for different periods at temps. below 400°. The contraction above 100° due to the formation of troostite was noted, and also the expansion above 210°, reaching a max. at 250° to 300°, due to decompn. of austenite, in steels of 0.58 to 1.57% C.

G. F. COMSTOCK

The microstructure of aluminum-iron alloys of high purity. E. H. DIX, JR. *Proc. Am. Soc. Testing Materials* (preprint) No 23, 10 pp (June, 1925).—Some constituent contg. Fe is present in all Al alloys of ordinary purity, and the study of such constituents is fundamental. Unusually pure Al was used for this work, the source of Fe was Armeo iron wire. The structures of alloys cast in various ways are discussed and illustrated by photomicrographs. Fe is practically insol in solid Al. A compd. FeAl<sub>3</sub> forms a eutectic with Al contg. about 17% Fe. In a well-polished specimen FeAl<sub>3</sub> appears bright with a slightly purple tinge. Alloys slightly in excess of the eutectic concn. show peculiar structures due to segregation when chill cast. Chill-casting from a high temp. (1100°) gave a very fine eutectic structure even with Fe as high as 3.4%, without primary FeAl<sub>3</sub>. Further work is planned to explain this. Specimens contg. only 0.06% Fe showed FeAl<sub>3</sub> under the microscope after annealing for 7 days at 640° to 645°. FeAl<sub>3</sub> has a strong tendency to coalesce during annealing. The best etching reagent is 1% (or weaker) HF in water, applied with cotton. If applied without swabbing, a little HNO<sub>3</sub> may be used to prevent tarnishing. The effects of other etching reagents are noted.

G. F. C.

The inner structure of alloys. WALTER ROSENHAIN. *Proc. Royal Inst. Gl. Britain* 24, 361-4(1925).—Alloys are composed either of solid solns or of intermetallic compds. X-ray examn. shows that in most solid solns the atoms of both metals are arranged indiscriminately on a single lattice. The substitution of solute atoms in the solvent lattice causes distortion. Where the distortion is general and slight on account of similarity of the two kinds of atoms, as in the harder metals, there is a wide range of soly. Distortion causes mechanical hardening, the hardening effect being roughly

inversely proportional to the solid soly. Distortion also accounts for the lower m. p. and higher elec. cond. of a solid soln. Diffusion in crystals occurs only when lattice distortion is produced in plastic metals by the diffusing atoms. Intermetallic compds. do not often enter into solid solns. The lattice form may change on account of an excess of dissolved atoms of a different kind. When more knowledge of the force fields surrounding atoms is obtained, it may be possible to predict the amt. of distortion produced in a given lattice by atoms of another metal in soln., and to calc. the equil. of simple and complex alloy systems. G. F. COMSTOCK

Standardization of methods of metallographic analysis of alloys. G. Z. NESSEL-STAUSS. *Commun. trav. sci. techn. effectués Rép. Russe* No. 8, 31-2(1922); *Rev. métal* 22(Extraits), 211-2(1925).—A plea for standardization to cover: chem. compn. and its relation to methods of manuf. and treatment, structure and the different internal constituents, nomenclature of the different constituents and elaboration of a rational classification of alloys, testing methods and their coordination. A. P. C.

Outline of the properties of white and colored alloys. I. A. KRILOV. *Congrès de Leningrad* (1924); *Rev. métal* 22(Extraits), 245(1925).—Brief comparison of the properties of anti-friction metals with high Sn content (90% or over) and of Frary-type metals with a plea for the standardization of anti-friction metals from the standpoints of their technical applications and conditions of use. A. PAFNEAU-COUTURE

Internal strain in brass and methods of relieving it. G. MASING AND C. HAASE. *Wiss. Veröffentl. Siemens-Konzern* 3, 22-33(1924).—After a review of the work of previous investigators on the season-cracking of brass, it is shown that simple cold rolling or rolling and bending does not always result in season cracking. If sheets of brass rolled from various thicknesses of annealed sheets down to a standard size are treated in the Erichsen machine, to obtain the greatest depression possible without visible signs of cracking, the sheets that were reduced in thickness 30-50% show the greatest tendency to season-cracking and require annealing at the highest temp. to overcome this. In all cases annealing at 225-250° for 30 min. is sufficient to remove the internal strain without decreasing the hardness. The tendency to season-cracking increases with the degree of rolling to a max. at 50% reduction in thickness, then decreases, it is also increased by the depth of the Erichsen depression. The residual strain in bent sheets of 63% Cu brass after annealing at low temps. increases with the amt. of distortion which the metal has suffered, and decreases linearly with rise of annealing temp., falling to zero at 300° (Cf. Moore and Beckinsale, *C. A.* 15, 1687; 16, 1734, 3294). B. C. A.

Lautal (aluminum-silicon-copper alloy). V. FUSS AND H. BÖHNER. *Z. Metallkunde* 17, 22-4(1925).—Lautal is an Al alloy contg. Si and Cu. The cast alloy has a tensile strength of 40 kg. per sq. mm., a Brinell hardness of 88, an elongation of 18-23%, an elec. cond. 40% of that of Cu and 70% of that of Al, and d. 2.74. Annealing at temps. above 150°, followed by quenching, results in a gradual diminution of hardness and tensile strength to minima of 50 and 24 kg. per sq. mm., resp.; further rise in the annealing temp. results in a partial recovery of hardness and tensile strength, the figures for these properties after annealing at 300° being 75 and 35 kg. per sq. mm., resp. After annealing and quenching from temps. above 350° the properties of the alloy may be improved by prolonged aging at 120°, the max. effect being obtained with an annealing temp. of 480-500°; no aging takes place at the ordinary temp. or in alloys annealed below 350°. The alloy may be welded readily and is easily forged at 480-500°; quenching and aging the forged alloy may increase its tensile strength to as much as 60 kg. per sq. mm., but its elongation is simultaneously reduced to 4%. Lautal is more resistant to corrosion than Al and most of its other alloys. B. C. A.

The metallurgical engineering of air-craft propeller hubs. W. J. MERTEN. *Trans. Am. Soc. Steel Treating* 7, 718-26(1925).—A detailed description of the design, mech. and metallurgical features. Cr-V steel contg. 0.45-0.55% C was used. The best heat treatment procedure is described. W. A. MUDGE

Recrystallization phenomena (in aluminum). H. RÖHRIG. *Z. Metallkunde* 17, 63(1925).—Annealing rolled sheets of Al at 220-350° results in rapid recrystn. and the growth of very large crystals differently oriented from those produced by annealing at a higher temp. This behavior is similar to that previously observed with Ag. B. C. A.

Softening of hard-rolled electrolytic copper. N. B. PILLING AND G. P. HALLIWELL. *Proc. Am. Soc. Testing Materials* (preprint) No. 24, 23 pp (June, 1925).—The annealing of Cu was studied for the purpose of finding how to obtain good ductility. An av. electrolytic Cu wire-bar was hot-rolled to a slab, and later cold-rolled to different reductions varying from 23 to 84%, the final thickness being less than 0.08 in. Anneal-

ing was done in an elec. furnace in nitrogen, or in oil or lead. Tensile tests were made on strips  $\frac{1}{4}$  in. wide, and the ductility was detd. by the elongation in 2 in. and the reduction in width. The results are expressed in tables and curves, and photomicrographs of the structures are shown. The rate of heating to or cooling from the annealing temp. is without effect on the strength or ductility. Annealing above 600° gives coarse grain and poor ductility. Softening at temps. between 200° and 300° begins very rapidly, being 80% complete within the first 7% of the time required for completion. No change in microstructure was recognized until a softening of 30% had occurred, and visible recrystn. occurs still later in the process of softening. Cu reduced 71% by cold-rolling softens 4 or 5 times faster than Cu reduced 53%, under the same conditions; and 84% reduction by cold-rolling gives 5000 times as rapid softening at 250° as 24% reduction gives. The softening rate increases extremely rapidly as the temp. rises, even at ordinary temps. there is a slow action constantly occurring, though 50 years may be required for a softening of 1%, whereas at 400° a few seconds may give complete softening. Prolonged heating at temps. below 500° causes only a slight decrease in strength and ductility, but at 900° the grain growth produced by long heating gives marked deterioration in ductility. The lowest practicable annealing temp. gives the best ductility. With less reduction in cold-rolling, the deterioration at high annealing temps. is less. The tensile strength decreases with increasing annealing temp. only below 600°, but the ductility decreases mostly above 500°. With a given annealing temp., Cu reduced more than about 60% in cold-rolling shows slightly increasing strength, but decreasing ductility. Ductility in general diminishes with increasing grain-size, yet the effect of initial cold-rolling persists, so that the ductility cannot be accurately estd. from the microstructure. G. F. C.

Action of iron on copper at high temperatures. P. SIEBE *Z. Metallkunde* 17, 19-21(1925).—Fe has no action on pure electrolytic Cu at any temp. below 1100° but ordinary "tough pitch" Cu which contains  $\text{Cu}_2\text{O}$  is rendered brittle and porous by heating in contact with Fe at temps. above 750°. This is due to the reducing action of the H and CO in the Fe, the action of the H is the greater as it readily diffuses into hot Cu, whereas CO has only a superficial action. B. C. A.

Fundamental factors in corrosion. G. M. ENOS *Ind. Eng. Chem.* 17, 703-7 (1925).—Data show the effect of C content, temp., time of exposure, and light upon the corrosion of steels in the atm. and in aq. solns. E. L. CHAPPELL

Accelerated corrosion tests on bare overhead electrical conductors. F. F. FOWLE. *Proc. Am. Soc. Testing Materials* (preprint 25) 1-16(June, 1925).—Samples of commercial wires and strands of steel, Cu, Al, copper-clad steel, galvanized steel, etc., were subjected in a test box to 800 eight-hour cycles of moisture, smoke and water spray. The appearance and tests of tensile strength show little corrosion of Cu and Al wires, no differences between solid and stranded wires, increase of corrosion resistance with carbon content of galvanized strands, and equal resistances for steel strands and copper-centered steel strands. E. L. CHAPPELL

The microscopic relations of sulfides and silica in blast-furnace and converter linings (PHEMISTER) 8.

Reducing ores. B. G. COBB U. S. 1,545,582, July 14. Coke, fluorspar and old slag or other non-electrolytic flux is fused by passing elec. current through it and maintained in fused condition by d. c. while the ore to be reduced, e. g., Bolivian Sn ore, is added.

Treating lead ores. V. MILLER and H. D. BALLOW U. S. 1,546,854, July 21. In cong. the Pb values of oxidized ores, the ore is heated to a temp. sufficient to convert the Pb carbonate content of the ore to oxide and then subjected to gravity sepa.

Extracting copper. T. J. TAPLIN and METALS PRODUCTION, LTD. Brit. 228,260, Oct. 31, 1923. In Cu-extn. processes similar to that of Brit. 220,720 (C. A. 19, 630),  $\text{Cu NH}_4$  carbonate soln. is used in the first stage contg. sufficient Cu in the cupric state to oxidize and render sol. all the Cu in the material. After this soln. is withdrawn the material is treated with an ammoniacal soln. contg. little or no Cu.

Hearth smelting furnace. H. BANSSEN and FACONETSEN-WALZWERK L. MANN-STAEDT & CO., AKT.-GES. Brit. 228,607, Nov. 3, 1923.

Rotary smelting furnace. A. MILLER and D. H. MILLER. U. S. 1,546,178, July 14.

Rotary furnace for producing wrought iron. E. F. BLESSING U. S. 1,546,964, July 21. U. S. 1,546,965 specifies puddling Fe by first agitating a broad shallow body of molten metal and slag and continuing the agitation during deepening and lateral reduction of the body, as may be done in the furnace specified in U. S. 1,546,964.

Cupola furnace. E. VANDERSTEIN. U. S. 1,546,521, July 21.

Refining iron or other metals. ELECTRO METALLURGICAL Co. Brit. 228,757, May 12, 1924. An alloy or aggregate for treating molten Fe, steel, bronze, Cu and other metals comprises Zr, Si and an element such as Mn, Ca or B which is capable of lowering the m. p. of zirconia-silica slag. Fe also may be present. A Zr-Mn-Si alloy is preferably produced by C reduction in an elec. furnace; or ferro-Mn may be fused with a Zr-Si-Fe alloy. Other examples also are given.

Deoxidizing open-hearth-steel baths. N. PETINOF and J. McCONNELL. U. S. 1,545,690, July 14. An open hearth alloy steel bath is treated with sufficient alloy of Al, Si and Fe (low in Si and in the form of a cast mass) to effect deoxidization of the steel. There is then added a ferro alloy of the metal or metals desired to make up the final compn. of the alloy steel, with sufficient additional quantities of the deoxidizing alloy to prevent reoxidation and to reduce any oxides present in the added metals.

Open-hearth-furnace operation. A. L. FEILD. U. S. 1,545,823, July 14. The bath in an open-hearth furnace is heated by burning a fuel gas with a gas contg. O in greater proportion than atm. air, and passing in contact with the inner surface of the furnace roof a preheated combustible gas and a preheated low-O gas so as to shield the roof from the destructive action of heat from the bath.

Titanium steel. W. MATHESIUS and H. MATHESIUS. U. S. 1,546,176, July 14. See Brit. 221,529 (C. A. 18, 812).

Zirconium steel. F. M. BECKER. U. S. 1,546,881, July 21. Zr is added to steel of high P content to counteract the detrimental effects of the P and increase the Izod impact number.

Material for carbonizing steel. S. B. MATHEWSON and W. K. JAMISON. U. S. 1,546,937, July 21. Scrap leather is placed in receptacles closed except for small holes in them, heated in a furnace and then allowed to cool in the furnace after the latter has been sealed except for natural draft.

Steel ingots. M. SAUNDERS. U. S. 1,546,796, July 21. In casting ingots the heat is retained in the upper portion of the ingot while the lower portion solidifies and sufficient downward pressure is applied to weld all portions of the ingot together.

Furnace for heat-treating steel gears, etc. F. T. CORZ. U. S. 1,545,485, July 14.

Nickel-copper alloy. J. W. LEHR. U. S. 1,545,838, July 14. A non-corrodible alloy adapted for uses similar to those of Monel metal comprises Ni 20-40, Sn 1-6% and Cu for the remainder, with substantially no Pb.

Lead alloys. SUMMIT CORPORATION. Brit. 228,345, Feb. 4, 1924. In forming bearing alloys or other Pb alloys, especially those also contg. Cu, molten Pb is treated with H<sub>2</sub> substantially free from O and then mixed with the other constituents of the alloy.

Lead-nickel-copper alloys. F. M. EKERT. Brit. 228,449, Aug. 5, 1924. Pb-Cu-Sn and Ni-Cu-Sn alloys are separately prepd. and combined to form a composite alloy which may contain Pb 20-70, Ni 10-30, Cu 10-50, Sn 1-20, Zn 1-10% and 0.25-5% each of P, Mn, Cr and W.

Aluminium alloy. T. HARADA. U. S. 1,546,657, July 21. An alloy which is resistant to corrosion comprises Cu 0.3-6.0, Ni 0.5-6.0 and Mn 0.5-6.0%, the rest being Al and impurities.

Heat-resisting alloys. A. W. NEARTCK. U. S. 1,546,852, July 21. In the formation of alloys of metals of widely different m. p., oxidation of the metal of lower m. p. is prevented by melting the metals separately and then pouring the metal of higher m. p. on to the other metal under such conditions as to prevent the slags of the 2 metals from coming into contact. This process is especially suitable for prepg. alloys contg. Al, Fe and Ni.

Cleaning and rust-proofing steel. J. D. KLINGER and C. L. BOYLE. U. S. 1,545,498, July 14. Steel is treated with a soln. formed of H<sub>2</sub>SO<sub>4</sub>, 1/2, a 5% aq. Na or K chromate soln. 4, alc. 4 1/2 and acetone 1 part.

Chemical-solution tank for use in cleaning metal articles. L. ROSENBERG. U. S. 1,545,979, July 14.

Coating metal pipes. GEISENKIRCHENER BEARBEITUNGS-ABT. GES. ABTEILUNG SCHALKE and H. PROJAHN. Brit. 228,529, Feb. 1, 1924. Fe pipes or the like made by centrifugal casting are enamelled, galvanized or tinned while they retain their casting heat.

Powdered zinc. E. H. GAUGHAN. U. S. 1,546,926, July 21. The size of Zn particles produced is varied by varying the adjustment of an injector by which molten Zn is atomized together with a gas such as compressed air.

Drawn tungsten wire. R. JACOBY. U. S. 1,546,899, July 21. A wire of small

crystals of metal of high m. p. such as W is transformed into wire of longer crystals by pushing it through a zone of high temp. in which it is heated to a point only slightly below its m. p.

## 10—ORGANIC CHEMISTRY

CHAS. A. ROULLER AND CLARENCE J. WEST

Action of ethyl hypochlorite upon mixed organo-magnesium compounds and upon magnesio-amines. J. F. DURAND AND R. NAVES *Bull. soc. chim.* 37, 717-23 (1925).—EtOCl,  $b_{75}$  36°,  $d_{-4}^{20}$  1.013, was prepd. by the method of Sandmeyer (*Z. physik. Chem.* 29, 613 (1899)), with some modifications of the technic. In the light, EtOCl decomps. rapidly with Cl evolution. With  $\text{PhMgBr}$ , PhCl is produced. With  $\text{PhNH MgBr}$ , EtOCl forms  $\text{PhN NPh}$ ,  $o\text{-ClC}_6\text{H}_4\text{NH}_2$  and  $p\text{-ClC}_6\text{H}_4\text{NH}_2$ . T. S. CARSWELL

Mixed dismutation of aldehydes. II. R. NAKAI *Biochem. Z.* 152, 258-75 (1924).—In the presence of  $\text{Mg(OMe)}_2$  or  $\text{Al(OR)}_3$ , the condensation of AcH and furfuraldehyde yielded iso-Am pyromucate,  $b_{11}$  111-15°,  $d$  1.0367. Furfuraldehyde and iso-PrCHO yielded furfuryl isobutyrate,  $b_{11}$  85-6°,  $d$  1.0313. Bromal and AcH yielded  $\text{CBr}_3\text{CH}_2\text{OAc}$ ,  $b_{17}$  109°,  $d$  2.2577, and  $\text{CBr}_3\text{CH}_2\text{O}_2\text{CCBr}_3$ , m. 69°,  $b_{17}$  206-7°. The action is regarded as a Cannizzaro reaction  $\text{RCH(OH)}_2 + \text{RCHO} \rightarrow \text{RCO}_2\text{H} + \text{RCH}_2\text{OH} \rightarrow \text{RCO}_2\text{CH}_2\text{R}$ , the aldehyde acting as an acceptor for H.  $\text{CBr}_3\text{CH}_2\text{OH}$  and  $\text{CCl}_3\text{CH}_2\text{OH}$  can be prepd. from AcH and bromal, by means of  $\text{Mg(OMe)}_2$ . F. A. CAJORI

The higher methyl ketones. G. T. MORGAN AND EUSEBIUS HOLMES *J. Soc. Chem. Ind.* 44, 103-10T (1925).—The Ba salts of the fatty acids of the general formula  $\text{C}_n\text{H}_{2n+1}\text{CO}_2\text{H}$ , where  $n = 7$  and 8, were prepd. by treating alc. solns. with the calcd. amt. of  $\text{Ba(OH)}_2$  and collecting the ppt. Where  $n = 10$  to 19, the Ba salts were prepd. by dissolving 1 mol. of the acid in alc., and adding 0.5 mol.  $\text{Na}_2\text{CO}_3$ , followed by 0.5 mol.  $(\text{AcO})_2\text{Ba}$ . The Ba salts were mixed thoroughly with 3 mols.  $(\text{AcO})_2\text{Ba}$  and distd. under vacuum. The resulting crude monoketones were purified by soln. in Et<sub>2</sub>O and EtOH, filtration, pptn. by  $\text{H}_2\text{O}$ , and repurified by crystn. as the  $\text{NaHSO}_4$  compds., which were subsequently decompd. by NaOH. The following ketones were prepd.:  $\text{C}_7\text{H}_{15}\text{COMe}$ ,  $b_{75}$  192°;  $\text{C}_8\text{H}_{17}\text{COMe}$ ,  $b_{75}$  209°, m. 14°;  $\text{C}_{10}\text{H}_{21}\text{COMe}$ , m. 27.5°;  $\text{C}_{11}\text{H}_{23}\text{COMe}$ , m. 39°;  $\text{C}_{12}\text{H}_{25}\text{COMe}$ , m. 48°;  $\text{C}_{13}\text{H}_{27}\text{COMe}$ , m. 52°;  $\text{C}_{14}\text{H}_{29}\text{COMe}$ , m. 55°; methyl nonadecyl ketone,  $\text{C}_{19}\text{H}_{39}\text{COMe}$ , m. 61°; methyl octadecyl ketone,  $\text{C}_{18}\text{H}_{37}\text{COMe}$ , m. 58°. The ketones were oxidized into the corresponding acids by slowly adding them at 0° to a mixt. of  $\text{H}_2\text{SO}_4$  and  $\text{Na}_2\text{Cr}_2\text{O}_7$ , and purifying the Ba salts. From the resulting acids the following ketones were prepd. as above:  $\text{C}_{10}\text{H}_{21}\text{COMe}$ , m. 20°;  $\text{C}_{11}\text{H}_{23}\text{COMe}$ , m. 33°;  $\text{C}_{12}\text{H}_{25}\text{COMe}$ , m. 43°. T. S. CARSWELL

The reducing action of organo-magnesium compounds. J. STAS *Bull. soc. chim. Belg.* 34, 183-90 (1925).—In the reaction of  $\text{PhMgBr}$  on  $\text{Pr}_2\text{CO}$  35% of tert. alc. is obtained while 10% of sec. alc. is formed by reduction,  $\text{MeCH:CH}_2$  (I) being given off. With iso-PrMgBr and iso-Pr<sub>2</sub>CO the reduction of the tert. alc. is complete, the off. sec. alc. and I being the only isolatable products. In the case of iso-PrMgBr and sec. alc. also the reduction is complete, the only products being I, EtOH, and iso-PrCO.Et also the reduction is complete, the only products being I, EtOH, and iso-PrCHO. An attempt was made to find a similar reduction product ( $\text{Me}_2\text{CHOH}$ ) from the reaction of iso-PrMgBr with  $\text{Me}_2\text{CO}$ , but although I equiv. to approx. 2% reduction could be detd., none of the sec. alc. could be isolated. WM. B. PLUMMER

Fulminic acid. VII. Polymerization of fulminic acid. Isocyanilic acid and erythrocyanic acid. HEINRICH WIELAND, ARTHUR BAUMANN, CURT REISENEGGER, WALTER SCHERER, JOHANNES THIELE, JULIUS WILL, HANS HAUSSMAN AND WALTER FRANK. *Ann.* 444, 7-40 (1925); cf. *C. A.* 7, 593.—Isocyanilic acid (I) (Scholvin. *J. prakt. Chem.* 32, 477 (1885)), prepd. according to S., is obtained in 1 g. yields from 1 kg. Hg fulminate. Prepn. from the Na salt and concd.  $\text{HNO}_3$  gives from 40 g. Hg salt 2-3 g. I (15-20%), m. 170-2° (decompn.); mol. wt. detns. establish the formula  $\text{C}_2\text{H}_2\text{O}_4\text{N}_4$  (analysis of the Ag and acid K salts); this formula is supported by the di-Bz deriv., m. 181° (decompn.) and the di-Ac deriv., m. 134°. With phenolphthalein it titrates as a monobasic acid. I is decompd. by long heating with HCl, giving  $\text{CO}_2$ ,  $\text{H}_2\text{C}_2\text{O}_4$ , HCN, 2 mols.  $\text{HN}_3\text{OH}$  and more than 1 mol.  $\text{NH}_3$ . Catalytic reduction did not give a homogeneous compd. I does not reduce  $\text{NH}_4\text{OH}\cdot\text{AgNO}_3$  or Fehling soln.  $\text{FeCl}_3$  gives no color reaction. I and  $\text{PhNH}_2\cdot\text{HCl}$  in boiling  $\text{H}_2\text{O}$  give the aniloxime of furoxandialdehyde (II), greenish yellow, m. 119°; the analogous phenylhydrazone, red-brown, m. 173° (decompn.). EtOH-NaOH and II give a compd.,  $\text{C}_{10}\text{H}_8\text{O}_4\text{N}_4$ , yellow,

m 145° (decompn.), which is probably not a stereoisomer but an open-chain compd. **I** and 2 *N* HCl give 50–60% of *cyanomethazonic acid*,  $\text{NCC}(\text{:NOH})\text{CH}_2\text{NO}_2$ , b. 70°;  $\text{NH}_4$  salt decomps 124°, gives a fleeting deep red  $\text{FeCl}_3$  reaction;  $\text{PhN}_2\text{Cl}$  gives a *phenylhydrazone*,  $\text{NCC}(\text{NOH})\text{C}(\text{NNHPh})\text{NO}_2$ , Au-yellow, m. 128° (decompn.). Acidifying the alk. soln gives an *isomeric acid*,  $\text{C}_6\text{H}_5\text{O}_2\text{N}_4$ , yellowish green, m 209° (decompn.), which is also formed from the free acid and  $\text{PhN}_2\text{Cl}$ . Treating **I** in the cold with dil alkali gives *hydratoisocyanilic acid* (**III**),  $\text{H}(\text{HON})\text{:CC}(\text{:NOH})\text{CHNO}_2\text{:C}(\text{:NOH})\text{H}$  m 187° (decompn.);  $\text{FeCl}_3$  gives a deep brownish red color; it does not react with  $\text{Br H}_2\text{O}$  and does not couple with  $\text{PhN}_2\text{Cl}$ . Heating with HCl splits off  $\text{H}_2\text{O}$ , giving epicyanilic acid,  $\text{C}_6\text{H}_5\text{O}_2\text{N}_4$ , m. 162° (decompn.);  $\text{FeCl}_3$  gives a red color. In the formation of **III**, there also results *metacyanilic acid*, m 70°, decomps 143°, whose  $\text{NH}_4$  salt is more sol than that of **III**. The acid gives no color with  $\text{FeCl}_3$ , but the  $\text{NH}_4$  salt gives a deep red color and also couples with  $\text{PhN}_2\text{Cl}$ , giving the compd.  $\text{C}_{10}\text{H}_8\text{O}_4\text{N}_4$ , yellow, m 143°. The acid also results by heating **I** with  $\text{Ba}(\text{OH})_2$  as the cryst. Ba salt. **I** and  $\text{SOCl}_2$  give 20% of *anhydroisocyanilic acid* (*cyanofuroxancarboxamide*),  $\text{C}_6\text{H}_5\text{O}_2\text{N}_4$ , m. 187° (decompn.);  $\text{PCl}_5$  in  $\text{Et}_2\text{O}$  gives a better yield. At a higher temp.  $\text{SOCl}_2$  gives 30–40% of *dicyanofuroxan*, m 42°, b. about 200°; it is very volatile and attacks the skin and eyes; it is very resistant to chem. agents. This compd also results from  $\text{NH}_4$  fulminate and concd  $\text{H}_2\text{SO}_4$ . While **I** in concd.  $\text{H}_2\text{SO}_4$  is pptd unchanged by  $\text{H}_2\text{O}$  after several hrs., addn. of  $\text{NaNO}_2$  gives *furoxandaldehyde*, whose *dianil*, light yellow, m 166° (decompn.). **I** results in 50% yields from  $\text{ClC}(\text{:NOH})\text{CH}(\text{:NOH})$  and  $\text{NaHCO}_3$ , and in 64% yields from *methazonic acid* and concd.  $\text{H}_2\text{SO}_4$ . **I** (3 g.) in 10 cc 50% KOH, warmed on a moderately boiling  $\text{H}_2\text{O}$  bath, the K salt pptd. with  $\text{EtOH}$ , and treated with 4 *N* HCl, gives 60–70% of *erythroisocyanilic acid*,  $\text{C}_6\text{H}_5\text{O}_2\text{N}_4$ , explodes 125°, mol wt. in isoquinoline 112, 103 (calcd., 190); it crysts with 1 mol.  $\text{H}_2\text{O}$  or  $\text{MeOH}$ ; *di-Na* salt, carmine red; *di-NH\_4* salt, bronze with 1 mol.  $\text{H}_2\text{O}$ ; Ag salt, dark green; Cu salt, olive-brown; Ba salt, dark red.  $\text{FeCl}_3$  gives a brownish red color. Definite reaction products could not be prepd from the acid. **I** (3 g.) and 15 cc. 50% KOH, concd. to a sirupy consistency, gives the K salt of *N*-hydroxytriazoledicarboxylic acid, carbonizes 222°, does not m. 300°. The mother liquors of the K salt contain the compd.  $\text{C}_{11}\text{H}_8\text{O}_4\text{N}_4$ , m 175° (decompn.), gives a brown  $\text{FeCl}_3$  reaction, and a Ag salt, insol. in dil  $\text{HNO}_3$ .

C. J. West

Action of phosphorus pentasulfide on alcohol. P. S. PRICHIMUKA. *J. Russ. Phys.-Chem. Sec* 56, 11–4(1925).—According to Kekulé  $\text{EtSH}$  is produced by the action of  $\text{P}_2\text{S}_5$  on  $\text{EtOH}$ .  $5\text{EtOH} + \text{P}_2\text{S}_5 = \text{P}_2\text{O}_5 + 5\text{EtSH}$ . According to Carius the reaction between  $\text{EtOH}$  and  $\text{P}_2\text{S}_5$  is:  $5\text{EtOH} + \text{P}_2\text{S}_5 = \text{H}_2\text{O} + \text{H}_2\text{S} + \text{Et}_3\text{PO}_2\text{S}_2 + \text{Et}_2\text{HPO}_2\text{S}_2$ . P finds that the equations of both K. and C. are incorrect. With anhyd.  $\text{EtOH}$  and  $\text{P}_2\text{S}_5$  he obtained di-Et dithiophosphate  $\text{SP}(\text{OEt})_2\text{SH}$ , which is a thick sirupy liquid sol in water,  $\text{H}_2\text{S}$ , free S, Et sulfides and some products which have not been exactly detd.  $\text{EtSH}$  is not a product of reaction between  $\text{P}_2\text{S}_5$  and  $\text{EtOH}$ , but results from decompn. of the  $\text{SP}(\text{OEt})_2\text{SH}$  at high temps.

BERNARD NELSON

**Taurine. I.** Methylation and acylation of taurine. MORITARO TEROAKA. *Z. physiol. Chem* 145, 238–43(1925).—*Dimethyltaurine*, m. 315–6°, was prepd. by refluxing a soln. of taurine with  $\text{MeI}$ ,  $\text{Na}_2\text{CO}_3$ , and  $\text{MgO}$  for 20 hrs. It forms a complex salt with  $\text{NH}_4\text{I}$  in the proportions of 2 **I**, contg.  $51\frac{1}{2}\%$   $\text{H}_2\text{O}$ . *Acetyltaurine Na*, m 233–4°, was prepd. by heating taurine in alc.  $\text{NaOH}$  with  $\text{Ac}_2\text{O}$ . The free base is unstable, decompg. into taurine and  $\text{AcOH}$ .

A. W. DOX

Attempts to prepare a hydroxyethylmethylmaleic acid. I. Derivatives of cyclopropanedicarboxylic acid. WILLIAM KÜSTER AND FRIEDRICH GRASNER. *Z. physiol. Chem* 145, 45–52(1925).—The formation of a methoxyethylmethylmaleic imide, in which the  $\text{MeO}$  is probably on the  $\alpha$ -C of the side chain, by oxidation of hematoporphyrin di-Me ether makes desirable the identification of this imide by synthesis, especially since oxidation of bilirubin gives a hydroxyethylmethylmaleic imide in which the OH is probably in the  $\beta$ -position. The scheme of synthesis attempted was: malonic ester  $\rightarrow$  cyclopropanedicarboxylic ester (**I**)  $\rightarrow$  *Et  $\beta$ -bromoethylmalonate* (**II**)  $\rightarrow$  *Ac deriv*  $\rightarrow$  *hydroxynitrile*  $\rightarrow$  *dehydration product*, but was unsuccessful because of the tendency of the **II** to revert to **I**. **II**, b. 132–4°, prepd. by satn. of **I** with dry  $\text{HBr}$  at 0°, is unstable, losing  $\text{HBr}$  under the influence of light and air and reverting to **I**. *Free acid*, m. 116°, by dissolving cyclopropanedicarboxylic acid in 66%  $\text{HBr}$ . *Me ester*, b. 216°, b. 150–2°, from the free acid and  $\text{CH}_3\text{N}$ . Treatment of **II** in  $\text{Et}_2\text{O}$  with  $\text{NH}_3$  gave the diamide and the ester-amide of cyclopropanedicarboxylic acid. *Cyclopropanedicarboxanilide*, m. 196°, by heating **II** with  $\text{PhNH}_2$ . This when sapond. with  $\text{HBr}$  gave *1-phenyl-5-pyrrolidone-4-carboxylic acid*, m. 64–5°, which after heating with Zn dust gives a strong pyrrole reaction. Condensation of  $\text{AcCH}(\text{CO}_2\text{R})_2$  with

$C_6H_5Br$  gave merely I and  $EtOAc$ . II. Derivatives of acetylcyclopropanecarboxylic acid. WILLIAM KÜSTER *Ibid* 53-68—A synthesis analogous to the above, but starting with  $AcCH_2CO_2R$  instead of  $CH_2(CO_2R)_2$ , also was attempted.  $Br(CH_2)_2AcCHCO_2R$  when shaken 24 hrs with 20%  $NH_4OH$  gave acetylcyclopropanecarboxamide (I), m.  $89^\circ$ , a ring closure as before. *Et* acetylcyclopropanecarboxylate semicarbazone m.  $126-7^\circ$ ; oxime m.  $77-8^\circ$ . Phenylhydrazone of I, m.  $137^\circ$ , when heated 15 min. at  $80^\circ$  with concd  $HCl$  gave 2 tautomeric 1-phenyl-3-dimethylene-4-methyl-2-pyrazolones, m.  $94^\circ$  and  $138^\circ$ , resp. Impure hydroxynitrile (II) of I was prepd by treatment of I in abs.  $Et_2O$  with  $KCN$  and concd  $HCl$ . It decmps when distd. at 6 mm. When heated with  $HBr$  12 hrs at  $130-40^\circ$  an intense odor of disubstituted malic acid derivs. developed. Extn of the product with  $Et_2O$  and distn gave a small fraction  $b_p$   $200-5^\circ$ , which from its Br content is believed to be a mixt. of 70%  $\beta$  bromoethylmethylmaleic anhydride (III) and 30% vinylmethylmaleic anhydride, and also hydroxyethylmethylfumaric lactone, m.  $202-3^\circ$ . Hydroxyethylmethylfumaric diamide, m.  $216^\circ$ , was obtained by passing  $NH_3$  into the  $Et_2O$  soln of the lactone. Monoamide, m.  $210^\circ$ , by evapn of the diamide with  $H_2O$ . The mixt obtained by sapon of II and distn. was dissolved in abs.  $Et_2O$  and satd. with  $HBr$  at  $0^\circ$  and a nearly pure prepn. of II obtained. This was treated with  $MeONa$ , and the product on distn gave 2 fractions  $b_p$   $155-60^\circ$  and  $220-5^\circ$ , resp., both of which contd. C, H and Me in agreement with the formula for methoxyethylmethylmaleic anhydride. They are not considered pure products, however, but are probably contaminated with a lactone ester or an itaconic acid deriv. A. W. DOX

Degradation of *l*- $\beta$ -hydroxybutyric acid. P. KARRER AND W. KLARER. *Helvetica Chim. Acta* 8, 393-5 (1925)— $MeCH(OH)CH_2CO_2Me$  and liquid  $NH_3$  in a sealed tube at room temp. for 60 hrs. give *l*- $\beta$ -hydroxybutyromide, m.  $99-100^\circ$ ,  $[\alpha]_D^{20} -22.49^\circ$  (0.221 g. in 8.6765 g. soln. in  $MeOH$ ). Br and  $Ba(OH)_2$  transform this into *l*-1-aminopropan-2-ol, the  $HCl$  salt of which has  $[\alpha]_D^{20} -58^\circ$ ; this is difficult to purify and was analyzed as the chloroplatinate, yellow, m.  $198^\circ$  (decompn.),  $[\alpha]_D^{20} -12.2^\circ$  (0.3898 g. in 13.4078 g. soln. in  $H_2O$ ). The free base has  $[\alpha]_D^{20}$  about  $-25.5^\circ$ . With  $AgNO_3$  this gives, in addn. to other products, *l*- $MeCH(OH)CH_2OH$ , with  $\alpha_D -1.518^\circ$  (1.02 g. in 12.4638 g. soln. in  $H_2O$ ); the amt. was not sufficient to purify further. C. J. WEST

Compounds of formaldehyde with glycine. MAX BERGMANN AND HELLMUT ENSSLIN. *Z. physiol. Chem.* 145, 194-201 (1925); cf. *C. A.* 18, 2129—The Cu salt of trimethylglycine crystals out when glycine Cu is warmed 15 hrs at  $50-2^\circ$  with an excess of 30%  $CH_2O$ . Krause's formula (*C. A.* 12, 2200) for this substance is erroneous. Methylene-glycine  $Ba + 5 H_2O$  was prepd. by treatment of trimethylglycine ester with  $Ba(OH)_2$  and also by K.'s procedure for his alleged hydroxytrimethylene-glycine  $Ba$ . All 5 mols. of  $H_2O$  are removed by drying *in vacuo* without otherwise altering the substance; hence it is a true methylene and not a hydroxymethyl deriv. A. W. DOX

Configuration of natural *l*-leucine. P. KARRER, W. JÄGGI AND T. TAKAHASHI. *Helvetica Chim. Acta* 8, 360-4 (1925).—*l*- $Me_2CHCH_2CH(NHBz)CO_2Et$  (35 g.) and  $MeMgI$  give 6.5 g. *l*-2,5-dimethyl-4-benzoylamino-5-hydroxyhexane (I), m.  $113^\circ$ ,  $\alpha_D^{18} -40.76^\circ$ ; it does not react with  $SOCl_2$  or  $PCl_5$ .  $EtO_2CCH_2CH(NHBz)CO_2Et$  (10.4 g.) and  $MeMgI$  give 3.2 g. *l*-2,5-dimethyl-2,5-dihydroxy-4-benzoylamino-hexane, m.  $148^\circ$ ,  $\alpha_D^{20} -16.4^\circ$  (0.16416 g. in 9.614 g. soln. in  $H_2O$ ). With  $SOCl_2$  there results *l*-2,5-dimethyl-5-hydroxy-4-benzoylamino-*l*-hexene,  $b_p$   $145-50^\circ$ , m.  $134^\circ$ ,  $\alpha_D -36.3^\circ$  (0.0182 g. in 2.20 g. of soln. in  $EtOH$ ). While the double bond is readily detected by  $KMnO_4$ , it could not be reduced to I. However, the double bond has no essential influence upon the rotation and specially upon the direction of rotation and so there is no doubt of the configuration of *l*-leucine, since that of *l*-asparaginic acid has been established (*C. A.* 18, 662). C. J. WEST

Further comparative studies on the oxidation of polypeptides and of 2,5-diketopiperazines. EMIL ABERHALDEN AND ERNST KOMM. *Z. physiol. Chem.* 144, 234-40 (1925)—Oxidation of glycine anhydride by means of 5%  $H_2O_2$  and  $FeSO_4$  catalyst 45 weeks in sunlight gave  $NH_2COCO_2NH_2$ . After boiling glycine anhydride and alanylglycine anhydride 0.5 hr. with 10%  $H_2O_2$ , the filtrates gave positive CO and ninhydrin reactions. After long boiling of glycine, leucine, glycylglycine, leucylglycine, leucyldiglycylglycine, silk peptone and gelatin with 10%  $H_2O_2$ , the reaction for CO was negative. When alanylglycine anhydride was boiled with  $H_2O_2$  in the presence of silk peptone, or silk peptone added after the boiling, the test was negative. Apparently a complex had been formed. The distinction between polypeptides and amino acid anhydrides is more pronounced when oxidation is performed with  $KMnO_4$  than with  $H_2O_2$ . A. W. DOX

Further studies on the structure of proteins. EMIL ABDERHALDEN AND ERNST KOMU *Z. physiol. Chem.* **145**, 303-15 (1925); cf. *C. A.* **18**, 2874.—From the hydrolyzate obtained by digesting edestin 3 weeks with pancreatic glycylproline anhydride, *m* 180-3°,  $[\alpha]_D^{20}$  -202°, was isolated by extrn. with Et<sub>2</sub>O. From dog hair after hydrolysis with 1% HCl 8 hrs at 150-60°, *alanylglycine anhydride*, *m* 235-7°, was obtained by extrn. with CHCl<sub>3</sub>. Hog bristles after hydrolysis with 1% HCl gave *alanylleucine anhydride*, *m* 233-8°, *alanylphenylalanine anhydride*, *m* 220-5°, and an *alanylleucine anhydride*, *m* 195°. The ratios of oxamide to decamination products after oxidation with Zn(MnO<sub>4</sub>)<sub>2</sub> were: silk peptone 1:0.84, keratin peptone 1:4.4, elastin peptone 1:3.7, 1:5.6.

Chemistry of creatinine. J. KAFFHAMMER *Biochem. Z.* **156**, 182-9 (1925).—The ester of creatine prep'd by Dox and Yoder (*C. A.* **17**, 726) is really a deriv. of creatinine. In creatine-HCl the alc. is firmly bound and no esters can be prep'd. F. A. C.

Condensation of aldehydes with the nitrile of aminomalonic acid. E. GRISHKEVICH-TROKHIMOVSKII AND A. SEMENTZOVA. *J. Russ. Phys.-Chem. Soc.* **55**, 547-8 (1924).—Upon polymerization moist HCN forms a comp'd, present up to 25%, which apparently is *aminomalonalonitrile*, NH<sub>2</sub>CH(CN)<sub>2</sub> (I). Heating of I with aldehydes in equimol. amts gave condensation products in good yields. With *BzH*: brown prismatic crystals of PhCH·NCH(CN)<sub>2</sub>, *m* 190° (decompn). With *o*-HOC<sub>6</sub>H<sub>4</sub>CHO: fine yellowish green needles of HOC<sub>6</sub>H<sub>4</sub>CH·NCH(CN)<sub>2</sub>, *m* 235° (decompn). With *p*-MeOC<sub>6</sub>H<sub>4</sub>CHO: yellow microcryst. powder of MeOC<sub>6</sub>H<sub>4</sub>CH·NCH(CN)<sub>2</sub>, *m* above 280°. In Et<sub>2</sub>O with BzCl a salt is formed, BzNHCH(CN)<sub>2</sub>·HCl which upon hydrolysis by H<sub>2</sub>O yielded BzNHCH(CN)<sub>2</sub> yellow crystals, *m* about 220° (decompn). H. B.

The action of nitrous acid on the nitrile of aminomalonic acid. E. GRISHKEVICH-TROKHIMOVSKII *J. Russ. Phys.-Chem. Soc.* **55**, 549-50 (1924).—Diazotization of NH<sub>2</sub>CH(CN)<sub>2</sub> (I), a trimeric deriv. of HCN (see preceding abstr.), produced large transparent yellow-orange crystals C<sub>3</sub>H<sub>3</sub>N<sub>3</sub> (II), *m* 145-50° (partial decompn, and sublimation), having strongly acidic properties which are apparently 1,2,3-triazole-4,5-dicarboxylonitrile, N:N C(CN) C(CN).NH, and upon sapon. with H<sub>2</sub>SO<sub>4</sub> give C<sub>3</sub>H<sub>3</sub>N<sub>3</sub>·

(CO<sub>2</sub>H)<sub>3</sub> (III), *m* 195-200° (decompn), slightly sol. in aq. HCl. Acid K salt; Cu salt, explosive. III gave upon dry distn 1,2,3-triazole; Ag and Bz deriv. identical with those described in literature. Sapon. II with aq. HCl produces the monoamide of III, does not *m* 275°.

Deriv. of II: C<sub>3</sub>H<sub>3</sub>N<sub>3</sub>Ag, white powder, stable in light, explodes upon heating; C<sub>3</sub>H<sub>3</sub>N<sub>3</sub>K, microcryst. powder, not deliquescent; C<sub>3</sub>H<sub>3</sub>N<sub>3</sub>(NH<sub>4</sub>); (C<sub>3</sub>H<sub>3</sub>N<sub>3</sub>)<sub>2</sub>Cu, sky-blue powder; (C<sub>3</sub>H<sub>3</sub>N<sub>3</sub>)<sub>2</sub>Ca·3H<sub>2</sub>O; C<sub>3</sub>H<sub>3</sub>Me, obtained from the Ag salt and MeI, *m* 57.5-8.5°. Sublimation of II gives colorless crystals of a substance, apparently isomeric with II. Structure of dicyanonitrizole. E. GRISHKEVICH-TROKHIMOVSKII AND L. KOTKE. *Ibid.* **55**:3.—The white modification of II (above) obtained by sublimation near the *m. p.* remains white when recrystd. from Et<sub>2</sub>O, turning yellow when crystd. from H<sub>2</sub>O. Attempts to disclose a difference in structure by prep'g. derivs. of either modification were frustrated. With CH<sub>3</sub>N<sub>3</sub> at 0° both were converted to the same methylidicyanonitrizole, any mol. rearrangement being excluded at so low a temp. Sapon. of II with 10% aq. NaOH at 70° produces *monocyanotriazolecarboxylic acid*, *m* 215-6° (decompn); Ag salt, white cheese-like ppt. At a higher concn and temp. II is converted to *monocyanotriazolecarboxylic acid*. C<sub>3</sub>H<sub>3</sub>N<sub>3</sub>Me sapon. with strong H<sub>2</sub>SO<sub>4</sub> gave acid (IV), *m* 202.5-3.5°, from whose Ag salt with MeI was obtained the Me ester (V), *m* 66-7°. Me ester (VI) of triazolecarboxylic acid, prep'd by this method, *m* 83.5-84°; a mixt. of V and VI *m* 55-60°. Conclusion: the Me group of IV is attached to N, therefore, also in C<sub>3</sub>H<sub>3</sub>Me. The investigation is being continued. H. BERNHARD.

Action of alkali on substituted uric acids. II. 1,3,7-Trimethyl-9-phenyluric acid. ELIZABETH STUART GATEWOOD *J. Am. Chem. Soc.* **47**, 2175-81 (1925); cf. *C. A.* **18**, 1816.—1,3,7-Trimethyl-9-uric acid (I) *m* 258-60°, thin plates,  $\alpha$  1.565,  $\gamma$  1.670, extinction, symmetrical,  $\alpha$ -parallel to elongation; interference figure, uniaxial, results in 2.2 g. yield from 5 g. phenyluric acid and 11.5 g. MeI and in about the same yield from Me<sub>2</sub>SO<sub>4</sub>, though the methylation can be carried out at a lower temp. and in much less time; or in 0.6 g. yield and in a few min. from 1,3-dimethyl 9-phenyluric acid and Me<sub>2</sub>SO<sub>4</sub>; the 7-Me and 1,7-di-Me derivs. methylate more slowly and are never completely methylated. Boiled with 50 cc. 2 N NaOH until the soln. was clear, 2 g. 1 gave 0.9-1.3 g. 1-methyl 3-phenylhydantoinmethylamide (II), needles, *m* 163-4°,  $\alpha$  1.555,  $\beta$  1.585,  $\gamma$  1.627; extinction, parallel,  $\gamma$ -parallel to elongation; interference figure, biaxial. The yields were not so good with *N* or 4 *N* alkali. NaOH (4 N) decomps. II, giving CO<sub>2</sub>. MeNH, and 1-methyl 3-phenylhydantoin, *m* 107-8°,  $\alpha$  1.515,  $\gamma$  1.665; needles; extinc-

tion, parallel,  $\gamma$ -parallel to elongation. Methylphenylhydantoic acid, m.  $150^\circ$  (not  $102^\circ$  as given by Paal and Gausen, *Ber* 28, 3233(1893)), plates, extinction, symmetrical,  $\alpha$ -parallel to elongation,  $\alpha$  1.530,  $\gamma$  1.625. Oxidation of II with 3%  $\text{H}_2\text{O}_2$  in KOH gives methylphenylhydroxyhydantoinmethylamide, crystg with 1  $\text{H}_2\text{O}$ , lost at  $100^\circ$ , and m.  $195-6^\circ$ , plates, extinction parallel,  $\gamma$ -parallel to elongation,  $\alpha$  1.510,  $\gamma$  1.620; this is decompd. by 4 N NaOH to  $\alpha,\beta$ -methylphenylurea, m.  $150^\circ$ , hexagonal plates, extinction, symmetrical,  $\gamma$ -parallel to elongation, interference figure, biaxial,  $\alpha$  1.600,  $\gamma$  1.715. Di-Et phenylureidomalonate, needles, m.  $112-4^\circ$ , extinction, parallel,  $\alpha$ -parallel to elongation,  $\alpha$  1.550,  $\beta$  1.610, from  $\text{H}_3\text{NCH}(\text{CO}_2\text{Et})_2$  and  $\text{PhCNO}$ , could not be transformed into Et 3-phenylhydantoincarboxylate, from which it was expected to obtain the amide. With  $\text{MeNH}_2$  it gives phenylureidomalonate methylamide, thin, hexagonal plates, m.  $225^\circ$ ; extinction, symmetrical,  $\beta$ -parallel to elongation, interference figure, biaxial,  $\beta$  1.598. 1,3-Dimethyl-9-allylpseudouric acid, octagonal plates, softens  $180^\circ$ , m.  $190^\circ$  (decompn.); extinction, symmetrical,  $\alpha$ -parallel to elongation,  $\alpha$  1.545,  $\gamma$  1.605, in 3 g. yield from 10 g. dimethyluramic and 5 g.  $\text{C}_2\text{H}_5\text{NCO}$ . Boiled with concd.  $\text{HCl}$  this gives 1,3-dimethyl-9-allyluric acid, rectangular plates, does not m.  $280^\circ$ , extinction, parallel,  $\alpha$ -parallel to elongation; interference figure, biaxial,  $\alpha$  1.665,  $\gamma$  1.730. III. 1,3,7,9-Tetramethyluric acid and 1,3,9-trimethyluric acid. *Ibid* 2181-9.—1,3,7,9-Tetramethyluric acid, needles and small plates; extinction, parallel,  $\alpha$ -parallel to elongation;  $\alpha$  1.435,  $\gamma$  1.710; 4 N NaOH gives 1,3-dimethylhydantoinmethylamide, thick needles, sinters  $175^\circ$ , m.  $179-80^\circ$ ; extinction, (1) parallel, (2) angle  $41^\circ$ ,  $\gamma$ -parallel to elongation; interference figure, biaxial;  $\alpha$  1.520,  $\beta$  1.565,  $\gamma$  1.645. Oxidation gives the 5-HO deriv., hexagonal plates, sinters  $155^\circ$ , m.  $164-5^\circ$ ; extinction, symmetrical,  $\alpha$ -parallel to elongation; interference figure, biaxial; large optic angle,  $\alpha$  1.460,  $\gamma$  1.590 (?). 1,3,9-Trimethyluric acid, hexagonal plates; extinction, symmetrical  $\gamma$ -parallel to elongation, interference figures, biaxial;  $\alpha$  1.525,  $\gamma$  1.705. Alkali gives 3-methylhydantoinmethylamide, hexagonal and octagonal plates, m.  $235-7^\circ$ ; extinction, symmetrical (octagonal),  $14^\circ$  (hexagonal),  $\alpha$ -parallel to elongation; interference figure, biaxial;  $\alpha$  1.485,  $\beta$  1.620,  $\gamma$  1.670. Oxidation gave the 5-HO deriv. (isocaffuric acid), m.  $194^\circ$ , extinction angle,  $35^\circ$ ,  $\gamma$ -parallel to elongation; interference figure, biaxial;  $\gamma$  1.555. An intermediate compd. that would show where the 1st break in the uric acid ring occurs could not be isolated. The causes of the varying stability of substituted uric acids towards alkali are discussed.

C. J. WEST

Hydrated mesotartaric acid. M. AMADORI. *Atti accad. Lincei* [vi], 1, 244-6 (1925); cf. C. A. 19, 1249.—The monohydrate of mesotartaric acid crystals, in pinacoidal tridinic crystals,  $a:b:c = 1.5461:1.12051$ ,  $\alpha = 83^\circ 13'$ ,  $\beta = 90^\circ 24'$ ,  $\gamma = 104^\circ 42'$ .

B. C. A.

Sugars from the standpoint of the organic chemist. J. C. IRVINE. *Proc. Roy. Inst. Great Britain* Feb. 27, 1925, 1-15.—An address on the investigation of the constitution of sugars, particularly glucose and cellulose.

A. PAPINEAU-COUTURE

Synthesis of the phosphoric acid esters. II. Syntheses of some glucose monophosphoric acid esters and their behavior toward yeast. SHIGERU KOMATSU and RIZUTSU NONZU. *Mem. Coll. Sci. Kyoto Imp. Univ.* Series 7A, No. 6, 377-87 (1924).—To 8 g. of pentaacetylglucose in 200 cc.  $\text{H}_2\text{O}$  at  $-5^\circ$  were added 50 g. of  $\text{Ba}(\text{OH})_2$ , then 5 g. of  $\text{POCl}_3$  in 50 cc. dry  $\text{Et}_2\text{O}$  drop by drop, with stirring, which was continued 3 hrs. The mixt. was made up to 800 cc. with  $\text{H}_2\text{O}$ , 32 g. of  $\text{Ba}(\text{OH})_2$  added, shaken for 24 hrs., filtered and the residue washed with  $\text{Ba}(\text{OH})_2$  soln. The residue was extd. 6 times with 400 cc. of  $\text{H}_2\text{O}$ , the exts. were combined, satd. with  $\text{CO}_2$  and filtered. The filtrate was concd. in *vacuo* to a small vol.,  $\text{BaCO}_3$  removed, and the soln. poured into abs.  $\text{EtOH}$ , pptg. the Ba glucose 1-monophosphate (I) ( $\alpha$  or  $\beta$ ) as a white powder. This, dried in *vacuo* at  $78^\circ$  over  $\text{P}_2\text{O}_5$  gave C, 17.70%; H, 2.97%; P, 7.64%; Ba, 34.70%; ash, 56.53% while the calcd. for  $\text{C}_6\text{H}_{11}\text{O}_5\text{PO}_3\text{Ba}$  is C, 18.21%; H, 2.81%; P, 7.84%; Ba, 34.73%; ash, 56.74% (as  $\text{Ba}_2\text{P}_2\text{O}_7$ ). It showed  $[\alpha]_D^{25} 14.9^\circ$ , reduced Fehling soln. only on prolonged boiling or after hydrolysis, gave an osazone m.  $203-4^\circ$ , was pptd. by alkali from  $\text{H}_2\text{O}$ , but not by  $\text{Pb}(\text{OAc})_2$ . To 5 g. of 1,2,5,6-diacetoneglucose in dry pyridine at  $-35^\circ$  were added 2.7 g. of  $\text{POCl}_3$  in pyridine,  $\text{Ba}(\text{OH})_2$  soln. to alkalinity, and the pyridine was distd. off in *vacuo*, the residue kneaded with  $\text{Ag}_2\text{SO}_4$  in a mortar (to remove Cl), the excess Ag removed with  $\text{H}_2\text{S}$ , excess  $\text{Ba}(\text{OH})_2$  added,  $\text{CO}_2$  passed in, the soln. filtered, the filtrate concd. to a small vol. in *vacuo* and poured into abs.  $\text{EtOH}$ . Overnight a gelatinous ppt. formed and was filtered off and dried over  $\text{CaCl}_2$ . The filtrate was concd. and dried over  $\text{CaCl}_2$ . Both products were mixed with diacetone glucose which was removed with  $\text{Et}_2\text{O}$ . Yield of residue, 6 g. dried at  $100^\circ$  over  $\text{P}_2\text{O}_5$ . Ba 1,2,5,6-diacetone-glucose 3-monophosphate (II). Analysis gave C, 29.98%; H, 4.40%; P, 6.64%; Ba, 27.74%; ash, 46.60%; calcd. for  $\text{C}_{12}\text{H}_{21}\text{O}_{10}\text{PO}_3\text{Ba}$ , C, 30.29%; H, 4.00%;

P, 6.53%; Ba, 28.89%; ash, 47.18%;  $[\alpha]_D^{25}$  6.80°. To remove  $\text{Me}_2\text{CO}$ , 2 g. of II was dissolved in 100 cc of 4 N  $\text{H}_2\text{SO}_4$  and kept at 40° for 24 hrs., neutralized with  $\text{BaCO}_3$ , made alk. with  $\text{Ba(OH)}_2$ , filtered, the filtrate concd. to 0.5 vol *in vacuo*, filtered, the filtrate concd. *in vacuo* to a small vol, and poured into abs EtOH, pptg. 1.1 g. of the Ba glucose 3 monophosphate (III), which was washed with 80% EtOH and dried over  $\text{CaCl}_2$  *in vacuo* and then over  $\text{P}_2\text{O}_5$  *in vacuo* at 78°. Analysis gave C, 18.22%; H, 3.27%; P, 7.25% and 7.38%; Ba, 33.45% and 31.17%; ash, 56.19%; calcd. (same as I);  $[\alpha]_D^{25}$  29.2° after 20 min and diminished slightly in 24 hrs. Dried glucose (16 g.) in 80 cc. of pyridine at -5° was vigorously stirred during the addn. of 12 g  $\text{POCl}_3$  in 30 cc of  $\text{CHCl}_3$  and for 3 hrs longer. Cold  $\text{H}_2\text{O}$  was added and the mixt. stirred overnight, the pyridine removed by vacuum distn., the residue dild. with  $\text{H}_2\text{O}$ , made alk. with  $\text{Ba(OH)}_2$ , filtered, Ba removed with  $\text{CO}_2$ , and the filtrate concd. *in vacuo* to a sirup. This was dild. with  $\text{H}_2\text{O}$ , treated with  $\text{Ag}_2\text{SO}_4$  and  $\text{H}_2\text{S}$ , air passed in to remove  $\text{H}_2\text{S}$ , the soln. filtered,  $\text{Ba(OH)}_2$  added,  $\text{CO}_2$  passed in, the  $\text{BaCO}_3$  removed and the filtrate concd. *in vacuo* and poured into abs EtOH (giving 75% EtOH). The Ba salt pptd. was centrifuged, washed with 75% EtOH and again centrifuged. The ppt. was dissolved in  $\text{H}_2\text{O}$ ,  $\text{Ba(OH)}_2$  added, the soln. filtered, pptd. with abs EtOH, the ppt. washed with 80% EtOH, dissolved in  $\text{H}_2\text{O}$ , filtered, and  $\text{CO}_2$  passed in. The ppt. Ba glucose 6-monophosphate (IV), dried as before gave C, 18.61%; H, 3.28%; P, 8.42%; Ba, 33.81%; calcd. same as I;  $[\alpha]_D^{25}$  19.1°, whence  $[\alpha]_D^{25} = 29.0^\circ$  for the free ester. The salt reduced Fehling soln. readily. The Ca salt of Neuberg's ester was prepd. by the action of  $\text{POCl}_3$  on glucose in the presence of  $\text{CaCO}_3$ . Dried over  $\text{H}_2\text{SO}_4$  it gave C, 21.82%; H, 4.23%; P, 9.69%; calcd. for  $\text{C}_6\text{H}_{11}\text{O}_5\text{PCa} \cdot 2\text{H}_2\text{O}$ , C, 21.55%; H, 4.49%; P, 9.28%;  $[\alpha]_D^{25}$  29.3° (after 20 min) and finally 25.0°, corresponding to 30.5° for the free ester. Hence this ester is identical with IV. The Na salts of the esters were prepd. by treating the Ba or Ca salts with the calcd. amt. of  $\text{H}_2\text{SO}_4$ , centrifuging off the sulfate and neutralizing with NaOH and phenolphthalein. None of the esters was fermented by brewers' yeast, while I and III were fermented rapidly with zymen (V), and they accelerated the action of V on glucose. III, after 4 days, started the action of V on glucose, with or without  $\text{Na}_2\text{HPO}_4$ . It is probable also that the hexose monophosphoric ester plays as important a role in the alc. fermentation of sugars as the diphosphoric ester does.

M. A. YOUTZ

**Synthesis of polysaccharides. I. Synthesis of an isotrehalose.** H. H. SCHLUBACH AND KURT MAUREN *Ber* 58B, 1178-84 (1925).—According to Hudson's calcn. (C A 10, 2230), Fischer and Debrück's synthetic isotrehalose is quite pure  $\beta$ ,  $\beta$ -trehalose (found  $[\alpha]_D^{25} -39.4^\circ$ ; calcd.  $-58^\circ$ ), while the natural trehalose (I) is the  $\alpha$ ,  $\alpha$ -form. Attempts by S. and M. to synthesize I by heating tetraacetylglucose (II) with HCl in  $\text{C}_6\text{H}_6$  under the most varied conditions of concn., time and temp. and in the presence of various dehydrating agents and catalysts never resulted in more than 10% condensation to a disaccharide, as measured by the decrease in reducing value according to Willstätter and Schudel's method (C A 13, 406); the rotations of the reaction products were quite irregular, and in many cases on long continued action a reverse cleavage of the disaccharide formed could be detected. No better results were obtained with  $\text{Et}_2\text{O}$  or  $\text{CHCl}_3$  as the solvent. II fused alone (without any solvent) undergoes no material change but in the presence of finely powd.  $\text{ZnCl}_2$  a 50% condensation can be effected. Exhaustive methylation of the product with alk.  $\text{Me}_2\text{SO}_4$  and distn. yields an octa-Me deriv. (III) of a disaccharide as a yellowish sirup, b. pt. 160°,  $n_D^{20}$  1.4626,  $[\alpha]_D^{20}$  82.8° (c 0.6100,  $\text{C}_6\text{H}_6$ ), becomes turbid on cooling but cannot be solidified. The octa-Me deriv. (IV) of natural I b. pt. 170°,  $n_D^{20}$  1.4598,  $[\alpha]_D^{20}$  199.8° (c 0.6260,  $\text{C}_6\text{H}_6$ ), also becomes turbid, without crystg., on cooling. On hydrolysis with 5% HCl at 98°, IV after 10 hrs. showed  $[\alpha]_D^{20}$  99.4° (c 0.9105,  $\text{C}_6\text{H}_6$ ), and after 6 hrs. more 100.5° (c 0.8214,  $\text{C}_6\text{H}_6$ ), while the value for 2,3,5,6-tetramethylglucose (V) is 99.0° (c 0.500,  $\text{C}_6\text{H}_6$ ); V was isolated, in cryst. form, in 75% yield. III, on the other hand, after 6 hrs. hydrolysis showed  $[\alpha]_D^{20}$  81.66° (c 0.4960,  $\text{C}_6\text{H}_6$ ), and after 2 hrs. more 80.47° (c 0.4660,  $\text{C}_6\text{H}_6$ ), and from the sirup only 17.5% cryst. V could be isolated; the non-solidified part of the product showed  $[\alpha]_D^{20}$  70.0° (c 0.9181,  $\text{C}_6\text{H}_6$ ), and possibly consisted essentially of  $\alpha$ ,  $\beta$ -trehalose, for which II calculates 70°. II. The galactosidoglucose of E. Fischer and E. F. Armstrong. H. H. SCHLUBACH AND WOLFGANG RAUCHENBERGER. *Ibid* 1184-9.—Armstrong (*The Carbohydrates and the Glucosides*, 4th ed., pp 133, 152 (1925)) and others believe that Fischer's synthetic galactosidoglucose (I) is identical with natural melibiose (II). S. and R., by exhaustive methylation with alk.  $\text{Me}_2\text{SO}_4$  (without previous fermentation) of the product of the reaction of acetochlorogalactose and glucose

obtained 6.8% of an octa-Me deriv. (III) of a disaccharide,  $b_{\text{max}}$  160°,  $n_D^{20}$  1.4660,  $[\alpha]_D^{20}$  8.39° (c 0.7149, H<sub>2</sub>O), -6.15° (c 1.1385, 96% alc.), -12.21° (c 0.9008, C<sub>6</sub>H<sub>6</sub>); if the primary condensation product is previously fermented according to F. and to A., the residual monosaccharides cannot be completely removed even by long continued action of the yeast (the part remaining unfermented is probably chiefly galactose); the disaccharide formed is also partly attacked and there is obtained only 2.6% of an octa-Me deriv. with  $[\alpha]_D^{20}$  12.92° (c 0.9676, 96% alc.) II yields an octa-Me deriv.,  $b_{\text{max}}$  163°, m. 98.5°,  $n_D^{20}$  1.4662,  $[\alpha]_D^{20}$  104.16° (c 1.0272, 96% alc.), 87.72° (c 1.0374, C<sub>6</sub>H<sub>6</sub>). I and II are therefore not identical. The const. of III are very similar to those of octa-methylactose (IV) but attempts to crystallize III by seeding with pure IV failed, and while hydrolysis of IV with 5% HCl at 80° stops after 5 hrs with  $[\alpha]_D^{20}$  90.9° (c 2.0244), that of III stopped after 6 hrs with  $[\alpha]_D^{20}$  55.87° (c 1.6308), 68.66° (c 2.2428). From III the galactose component could easily be isolated as the crystalline anilide of 2,3,4,6-tetra-methylgalactose; the difference between the rotations of the hydrolysis products of III and IV must therefore be due to the glucose component, and as a matter of fact from III was obtained a trimethylglucose (V) with  $[\alpha]_D^{20}$  35.8° (c 1.200, MeOH), while the 2,3,6-trimethylglucose from lactose shows  $[\alpha]_D^{20}$  83.6° and the 2,3,5-deriv. from II has  $[\alpha]_D^{20}$  61.7° (c 2.123, MeOH).

C. A. R.

Lichen starch. HANS PRINGSHERM *Z. physiol. Chem.* 144, 241-5 (1925).—The statement of Karrer and Joos (*C. A.* 19, 1853) that isolichenin is a mixt. separable into 2 components with rotations of 88° and 148°, resp., one of which contains mannan, is refuted. A repetition of P.'s work yielded a product with a rotation of 188.2°, and from it a quant. yield of maltose was obtained by hydrolysis with diastase. A. W. D.

Irisin and the enzymic cleavage of polyfructosides. HANS V. EULER and HOLGER ERTDMANN *Z. physiol. Chem.* 145, 261-75 (1925).—Irisin, prepd in 13-15% yield from iris tubers, m. 205-10°, decomps. 215-8°,  $[\alpha]_D^{20}$  -52.10°, and by the diffusion method shows a mol. wt. of 10,300. Heated with Ac<sub>2</sub>O and pyridine it gives *irisin triacetate* (I), m. 206-8°,  $[\alpha]_D^{20}$  -22.70°. Cleavage of I by heating with PhNHNH<sub>2</sub> gives a non-reducing, N-free product,  $[\alpha]_D^{20}$  -49-50°, which is not hydrolyzed by yeast, emulsin or sucrase. Irisin forms Na and Ba salts. The ppt. with Ba(OH)<sub>2</sub> has the compn. 0(C<sub>6</sub>H<sub>4</sub>O<sub>4</sub>).Ba(OH)<sub>2</sub>. Irisin is hydrolyzed by HCl at approx. the same rate as sucrose, inulin and sinistrin. It is not hydrolyzed by Taka-diastase, whereas inulin is very slowly hydrolyzed. It is possible that the 2 fructosides contain the fructose in different metamerie forms ( $\beta$  and  $\gamma$ ) or with different ring structures. A. W. DOX.

Toxins. II. Croton. P. KARRER, F. WEBER and J. VAN SLOOTEN. *Helvetica Chim. Acta* 8, 384-92 (1925); cf. *C. A.* 18, 2717.—Croton comprises about 0.36% of the croton seed; the seed powder is extd. with 10% NaCl for 2 days, the ext. dialyzed for 8 days, the globulin filtered off and the crude croton pptd. by (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>; this is dissolved in H<sub>2</sub>O, filtered, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> added, the ppt. filtered and again dissolved in H<sub>2</sub>O and dialyzed; evapn. gives a yellowish brown to grayish black amorphous powder. Agglutination and hemolytic expts. are reported. Croton behaves towards kaolin as does ricin; it is best fractionated by basic Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>[Al(OH)<sub>3</sub>]. A product with 3.34% ash (mostly Ca, but some Li, S, P and Cl) and with  $[\alpha]_D^{20}$  -2.143° in 1% soln. was hydrolyzed with dil. H<sub>2</sub>SO<sub>4</sub>; total N, 13.17%; amide N, 1.50; humin N, 0.2; total N of mono-NH<sub>2</sub> acids, 7.14; of diamino acids, 3.14; arginine N, 1.14; N in residue from arginine, 2.70; the following NH<sub>2</sub> acids were isolated: alanine, 3.49; valine, 0.23; leucine, 22.05; tyrosine, 4.57; cystine, 0.88; proline, 1.78; aspartic acid, 1.70; glutamic acid, 3.70; arginine, 1.71; lysine, 3.53; histidine, 0; peptide-anhydride, 0.85; unidentified, 10.68; humin substances, 8.54; insol. mineral substances, 0.58; total, 65.39. C. J. W.

The constitution of nucleic acids. An outline of some relations among phosphorus-containing principles of the tissues. MAURICE TARRILLIER *Bull. soc. chim.* 37, 569-93 (1925).—A review.

HARRIET W. GIBSON

Structure of benzene. N. SCHOORL. *Chem. Weekblad* 22, 343 (1925); cf. van Laar, *C. A.* 19, 2480.—It has been overlooked by most chemists that the mol. refraction of benzene is not in harmony with Kekulé's formula since it accounts for the presence only of 3 double bonds but not for the fact of their being conjugated. The refraction should be 50.7 instead of 44.7, 2 being according to Brühl the increase for one conjugated double bond.

MARY JACOBSEN

Electrochemical oxidation of iodobenzene, o-iodotoluene. FR. FICHTER and PAUL LOTTER. *Helvetica Chim. Acta* 8, 438-42 (1925).—PhI, oxidized in dil. H<sub>2</sub>SO<sub>4</sub> with PbO<sub>2</sub> anodes and 0.02 amp./cm.<sup>2</sup>, gives with a diaphragm O C<sub>6</sub>H<sub>4</sub>:O and HIO<sub>3</sub>;

without a diaphragm,  $p\text{-C}_6\text{H}_4(\text{OH})_2$  and I. The yields are poor. In  $\text{AcOH-H}_2\text{SO}_4$  there results  $\text{PhIO}$ ,  $\text{AcOH-HClO}_4$  gives the same product, but if the time of the electrolysis is extended or the current or temp. raised, more and more  $p\text{-C}_6\text{H}_4\text{I}_2$  is formed. In  $\text{AcOH}$  alone, with Pt anodes and 0.05 amp./cm.<sup>2</sup>, there results 31.8% of  $\text{PhIO}$  from the  $\text{Ac}$  deriv.  $\text{PhI}$  (5 g.) in 100 cc 70%  $\text{AcOH}$ , Pt anodes, 0.08 amp./cm.<sup>2</sup>, gives 3.2 g.  $\text{PhIO}_2\text{Ac}$ , 0.3 g.  $\text{PhIO}$  and 2 g. unchanged  $\text{PhI}$ .  $o\text{-MeC}_6\text{H}_4\text{I}$  in dil.  $\text{HCl}$  gives a poor yield of  $o\text{-IC}_6\text{H}_4\text{CHO}$  and  $o\text{-IC}_6\text{H}_4\text{CO}_2\text{H}$ ; in 70%  $\text{AcOH}$  there results some  $o\text{-OIC}_6\text{H}_4\text{CO}_2\text{H}$ , decomps.  $223^\circ$ .  $o\text{-IC}_6\text{H}_4\text{CO}_2\text{H}$  in 70%  $\text{AcOH}$  gives 82.7%  $o\text{-iodosobenzoic acid}$ , decomps.  $225^\circ$ .  $p\text{-IC}_6\text{H}_4\text{Me}$  in dil.  $\text{AcOH}$  gives  $p\text{-IC}_6\text{H}_4\text{CHO}$  and  $p\text{-IC}_6\text{H}_4\text{CO}_2\text{H}$ . In 70%  $\text{AcOH}$  there results a poor yield of  $p\text{-IOC}_6\text{H}_4\text{CO}_2\text{H}$ , exploding at  $222.5^\circ$ .

C. J. WEST

**Chlorosulfonic esters.** WILHELM TRAUBE *Z. angew. Chem.* **38**, 441-4 (1925).—The reaction of  $\text{ClSO}_3\text{Et}$  upon  $\text{PhNH}_2$  yields a mixt. of  $\text{PhNH}_2\text{Et}$  and  $\text{PhNEt}_2$ , as well as  $\text{PhNMeSO}_3\text{H}$ , the proportions depending upon the conditions of the expts.; yields for several conditions are reported.  $\text{PhNEtSO}_3\text{Na}$  may be alkylated by  $\text{ClSO}_3\text{R}$ , alkyl halides or sulfates in aq. solns.  $\text{PhNH}_2$  may be converted into  $\text{PhNHSO}_3\text{Na}$  and thus methylated, giving 85-90%  $\text{PhNMe}$ . Aliphatic amines react with  $\text{ClSO}_3\text{R}$  to give principally alkyl derivs.;  $\text{NH}_3$  gives mainly monoalkyl derivs.  $\text{PhOEt}$  or  $\text{PhOMe}$  is obtained in 75% yield from  $\text{PhOH}$ ,  $\text{ClSO}_3\text{R}$  and 30%  $\text{NaOH}$ . Other reactions are reported.  $\text{ClSO}_3\text{R}$  and  $\text{HCl}$  give  $\text{RCI}$ , the yield depending upon the concn of the  $\text{HCl}$ ; thus,  $\text{ClSO}_3\text{Et}$  and 6%  $\text{HCl}$  give 61.7%  $\text{EtCl}$ ; 12%  $\text{HCl}$ , 66.8; 24%  $\text{HCl}$ , 83.7; fuming  $\text{HCl}$ , 91%  $\text{EtCl}$ . With  $\text{HBr}$  there results up to 50% of  $\text{EtBr}$ . C. J. WEST

**Infra-red absorption spectra of organic derivatives of ammonia.** I. Aniline and some mono- and dialkylanilines. F. K. BELL *J. Am. Chem. Soc.* **47**, 2192-207 (1925).—The absorption spectra, between 1 and  $12\mu$ , are recorded for  $\text{PhNH}_2$ ,  $\text{PhNHMe}$ ,  $\text{PhNMe}_2$ ,  $\text{PhNH}_2\text{Et}$ ,  $\text{PhNEt}_2$ ,  $\text{PhNMeEt}$ ,  $\text{PhNHPr}$ ,  $\text{PhNPr}_2$ ,  $\text{PhNHBu}$ ,  $\text{PhNBu}_2$ , and  $\text{PhNH(iso-Am)}$ . With progressive substitution of the 3 H atoms of  $\text{NH}_2$  with first the  $\text{Ph}$  group and then alkyl groups, the sp. influence of the tervalent N on the absorption in the region of  $2.8\mu$  is progressively diminished until it is practically absent in the tert.  $\text{NH}_2$  group. Between  $2.7$  and  $3.4\mu$  the absorption reveals a pronounced qual. differentiation between  $\text{PhNH}_2$  and mono- and dialkylaniline. C. J. WEST

**Directive influence of substituents in the benzene ring.** II. The relative rates of bromination of certain  $o$ -,  $m$ - and  $p$ -isomers. A. W. FRANCIS, A. J. HILL AND JOHN JOHNSON *J. Am. Chem. Soc.* **47**, 2211-32 (1925); cf. *C. A.* **19**, 257.—A method is developed by which the relative rate of the several successive steps in the bromination of certain aromatic amino and phenolic compds. in acid aq. soln. may be estimated by detg. the wt. of the highest brominated product pptd. by various proportions of  $\text{Br}$ . Somewhat similar expts. were carried out in which 2 compds. compete for insufficient amts. of  $\text{Br}$ . From the results of such competitions, combined with the results of the partial bromination of each compd. singly, the relative velocity of each step of bromination of the series of compds. may be estimated. In this way about 100 velocity consts. were evaluated. The relative accelerative (or retarding) effect of the presence of certain groups, as derived from these consts., is in general accord with that given by previous authors and the data indicate that the so-called directive influence is less easy to specify than has by many been supposed. In  $\text{PhNH}_2$  and in all the  $m\text{-NH}_2$  compds. investigated, 2 of the substitutions of  $\text{Br}$  (but never 3, except in  $m\text{-C}_6\text{H}_4(\text{NH}_2)_2$ ) are simultaneous, but in no case (except  $m\text{-C}_6\text{H}_4(\text{OH})_2$ ) does a phenolic compd. behave in this way. This suggests that in the former case the 2  $\text{Br}$  atoms are substituted first in the  $\text{NH}_2$  group and thence by interchange go into the ring, whereas phenolic compds. can substitute only 1  $\text{Br}$  at a time in the directing group. This view is supported by the relatively slow rate of successive bromination of  $\text{PhNEt}_2$  and  $\text{PhOMe}$ , neither of which is brominated quant. The rate of substitution of the 1st  $\text{Br}$  atom in the  $o$ -isomer is always greater than in the  $p$ -isomer; in the latter the  $\text{Br}$  enters an  $o$  position, in the former, probably a  $p$ -position. On the other hand the rate for the 2nd atom may be greater than that for the 1st in a  $p$ - but in no case for an  $o$ -compd. When each of the 2 groups attached to the ring tends to direct the entering group to the  $o$ - or  $p$ -position with respect to itself, the  $m$ -isomer has the highest 1st velocity const.; but when one of these groups is of those generally recognized as  $m$ -controlling, the 1st const. for the  $m$ -isomer is lower than for the  $o$  or  $p$ . When both of the groups are  $\text{NH}_2$  or  $\text{HO}$ , the effect is still more marked, when they are  $m$  to each other, the rate is very much enhanced, but when they are in the  $p$ -position, the rate appears to be very slow. The original should be consulted for the mass of exptl. detail. C. J. WEST

**Synthesis of  $N,N'$ -dimethylenesulfonates of  $o$ -,  $m$ - and  $p$ -diaminoarsenobenzene.** KOZO KASHIMA *J. Am. Chem. Soc.* **47**, 2207-11 (1925).—Reduction of  $2\text{-O}_2\text{NC}_6\text{H}_4\text{N}_2$

$\text{AsO}_2\text{H}_2$  (I) in MeOH with 4% Na Hg gives 75% of  $2\text{-H}_2\text{NC}_6\text{H}_4\text{AsO}_2\text{H}_2$  (II), m. 153–4°. Reduction of I with  $\text{Na}_2\text{S}_2\text{O}_4$  or of II with  $\text{H}_3\text{PO}_2$  gives  $(\text{H}_2\text{NC}_6\text{H}_4\text{As})_2$ , yellow, decomp. 115–25°. Its  $N,N'$ -methylsulfonic acid forms a light red powder.  $3,3'$ -Diaminoarsenobenzene, yellow powder; di-HCl salt, gray ppt. Di-Na  $3,3'$ -diaminoarsenobenzene- $N,N'$ -dimethylenesulfonate, brownish yellow ppt. The corresponding  $4,4'$ -diamino deriv. is a reddish yellow powder; it reduces I solns but not indigo carmin.

C. J. WEST

**Organometallic bases.** FR. HEIN AND H. MEININGER. *Z. anorg. allgem. Chem.* 145, 95–116 (1925).—Several alkyl- and aryl-substituted metallic hydroxides have been made previously and described as strong bases. A systematic study of these has been made by means of elec. cond. in  $\text{H}_2\text{O}$  and in MeOH at various concns. The org. Hg bases increase in strength in the order  $\text{PhHgOH}$ ,  $\text{EtHgOH}$ ,  $\text{MeHgOH}$ ,  $p\text{-MeOC}_6\text{H}_4\text{HgOH}$ ,  $p\text{-Me}_2\text{NC}_6\text{H}_4\text{HgOH}$ , all being stronger than  $\text{PhNH}_2\text{OH}$ , but weaker than  $\text{NH}_4\text{OH}$  except at high concns. The org. Sn bases,  $\text{R}_2\text{SnOH}$ , were analogous but still weaker. The Ti bases,  $\text{R}_2\text{TiOH}$ , were much stronger, approaching NaOH, but falling below  $\text{TiOH}$ . The Cr bases,  $\text{Ph}_3\text{CrOH}$ ,  $\text{Ph}_2\text{CrOH}$ , and  $\text{PhCrOH}$ , decreasing in that order, also were very strong.  $\text{Et}_3\text{PbOH}$  is about as strong as  $\text{NH}_4\text{OH}$ . All the above bases are much stronger than the corresponding normal inorg. hydroxides. This is explained by application of the Pfeiffer-Werner aquobase theory, one OH group receiving all the basic force of the metal.

A. W. FRANCIS

The influence of methyl and sulfo groups, as well as other substituents, on the color of azo dyes. ERICH WANNER. *Z. anorg. Chem.* 38, 513–9 (1925).—In the case of substantive dyes, the position of the substituting Me groups exercises more influence than their no. The  $o$ -position has the greatest influence, the  $p$ -less, and the  $m$ -very little; 2 groups in the  $m$ -are weaker than 1 in the  $p$ -position. The addn. of Me groups increases the fastness to alkali, and complete fastness to dil. NaOH is reached when 2 Me groups are substituted in the diazo component. The position of the Me group is of little importance. The introduction of Me groups slightly increases the fastness to light. The introduction of  $\text{SO}_3\text{H}$  usually produces a positive color change, though in some cases a negative change was observed. The  $\text{SO}_3\text{H}$  group has little influence on the fastness to alkali or acid, but it does increase the fastness to light, the  $p$ - is much more effective than the  $m$ -position. The MeO group exerts a strong positive color change, and increases the fastness to alkali greatly, at the same time the fastness to light is greatly reduced. The  $\text{NO}_2$  and  $\text{NH}_2$  groups have a great influence on the color, but little influence on the fastness to alkali or light. When Cl is substituted in the aromatic nucleus, a slight negative color change takes place; when it is substituted in the Me group, a positive change occurs. Cl has no influence on the fastness to alkali and decreases the fastness to light.

T. S. CARSWELL

Some new substituted benzyl esters. CHARLES BARKENBUS AND J. B. HOLTZCLAW. *J. Am. Chem. Soc.* 47, 2189–92 (1925).—An attempt was made to prep  $\text{HO}-\text{CC}_6\text{H}_4\text{CH}_2\text{O}_2\text{CPb}$  with the idea that this would form a sol. salt which would be superior to  $\text{BzOPb}$ . The ester could not be obtained pure.  $p\text{-CNC}_6\text{H}_4\text{CH}_2\text{Cl}$  is obtained in 53.7% yield by chlorinating  $p\text{-CNC}_6\text{H}_4\text{Me}$  at 120–30° (about 2 hrs. in the light of a W lamp). Working up the mother liquor gave a total yield of 70%.  $o\text{-CNC}_6\text{H}_4\text{Me}$  at 140–50° gave 61.7% of  $o\text{-CNC}_6\text{H}_4\text{CH}_2\text{Cl}$ . Heating  $p\text{-CNC}_6\text{H}_4\text{CH}_2\text{Cl}$  6 hrs. with 50%  $\text{H}_2\text{SO}_4$  gives 76.5% of  $p\text{-HO}-\text{CC}_6\text{H}_4\text{CH}_2\text{Cl}$ , which is hydrolyzed by NaOH, giving 72.9%  $p\text{-HO}-\text{CC}_6\text{H}_4\text{CH}_2\text{OH}$ . A neutral solu. of  $\text{NaO}-\text{CC}_6\text{H}_4\text{CH}_2\text{Cl}$ , boiled for 10 min., gives 52% of  $p$ -carboxybenzyl- $p$ -chloromethyl benzoate, m. 221°, and about half that amt. of  $p\text{-HO}-\text{CC}_6\text{H}_4\text{CH}_2\text{OH}$ .  $o\text{-CNC}_6\text{H}_4\text{CH}_2\text{Cl}$  and  $\text{AcONa}$  in  $\text{H}_2\text{O}$ , heated at 100–10° for 5 hrs., give 56%  $o$ -cyanobenzyl acetate, b<sub>p</sub> 180–2°; benzoate, m. 54–5° (yield, 34.8%).  $p$ -Carboxybenzyl acetate, m. 123–4° (yield, 58.6%). Attempted hydrolysis of  $o\text{-CNC}_6\text{H}_4\text{COAc}$  in the presence of EtOH gave only  $\text{AcOEt}$  and phthalide.

C. J. WEST

Salts of several aromatic carboxylic acids and their solubility. FRITZ EPFRAM AND ALFRED PRISTER. *Helvetica Chim. Acta* 8, 369–83 (1925); cf. C. A. 19, 2482.—The following figures represent the mols. of  $\text{H}_2\text{O}$  of crystn., g. anhyd. salt in 1 l.  $\text{H}_2\text{O}$  at 20° and normality of the soln. (g. atoms metal in 1 l.); for details as to color of salts, etc., the original should be consulted. Benzoic acid: Mg, 4, 63.64, 0.239; Mn, 2, 48.20, 0.162; Sr, 1, 49.53, 0.150; Ba, 2, 49.55, 0.130; Ca, 2, 28.27, 0.100; Cd, 2, 33.40, 0.094; Zn, 1, 20.48, 0.067; Ni, 3(6), 12.91, 0.043; Co, 4, 10.13, 0.034; Ag, —, 2.17, 0.0095; Hg, 1, 2.03, 0.0047; Pb, 1, 1.79, 0.0040; Cu, 4, 1.00, 0.0033. Cinnamic acid: Mg, 2, 12.25, 0.0384; Sr, 4, 14.00, 0.0367; Ca, 3, 3.40, 0.0102; Co, 2, 3.02, 0.0086; Ni, 2, 2.93, 0.0083; Mn, 2, 2.14, 0.0061; Zn, 2, 1.50, 0.0042; Pb, 2, 1.41, 0.0023; Ba, 2, 0.444, 0.0010; Cd, 2, 0.374, 0.00092; Cu, —, 0.304, 0.00085; Ag, —, 0.212, 0.00083. 4-Nitrobenzoic acid: Ca, 6, 25.48, 0.068; Mg, 6, 18.40, 0.052; Mn, 6, 13.41, 0.035; Sr, 8, 13.40, 0.032; Co,

6 8 93, 0 023, Ni, 8, 7 77, 0 020, Zn, 2, 5 56, 0 014; Cd, 2, 4 45, 0 010; Ag, 0, 1 70, 0 0062; Cu, 1, 1 61, 0 0041, Ph, 0, 1 59, 0 0030, Ba, 0, 1 27, 0 0027. 4-Chlorobenzoic acid: Co, 4, 17 20, 0 046, Sr, 4, 13 41, 0 034; Mn, 2, 11 57, 0 027; Ca, 3, 7 37, 0 021; Cd, 2, 7 79, 0 0184, Ni, 4, 6 60, 0 0178, Zn, 2, 6 49, 0 0172; Cu, 2, 1 92, 0 0051; Ag, 0, 1 08, 0 0041; Ba, 1, 1 09, 0 0024, Pb, 2, 0 78, 0 0015. 4-Hydroxybenzoic acid: Sr, 1, 110 98, 0 307; Ca, 4, 83 66, 0 254, Mn, 8, 32 24, 0 101; Zn, 8, 16 87, 0 050, Co, 7, 12 54, 0 038; Ni, 7, 8 71, 0 021, Ag, 3, 2 72, 0 011; Pb, 2, 4 70, 0 0097, Ba, 2, 3 67, 0 0074; Cu, 7, 2 42, 0 0071. 4-Methoxybenzoic acid: Ca, 3, 25 25, 0 073; Sr, 1, 16 975, 0 044; Mn, 3, 14 52, 0 0406, Zn, 1, 11 74, 0 0319; Co, 3, 9 934, 0 0275; Cd, 1, 4 02, 0 0097; Ag, 0, 0 518, 0 0020, Ba, 1, 0 752, 0 0017; Pb, 1, 0 486, 0 0009. C. J. West

Metal compounds of the enol forms of monocarbonyl compounds and their use for syntheses. III. Action of carbon monoxide on ketone and ester enolates. HELMUTH SCHEIBLER AND OTTO SCHMIDT. *Ber* 58B, 1189-97(1925); cf. *C. A.* 16, 3067. As compared with the relatively stable metal derivs of enolized 1,3-di-C:O compds. ( $\beta$  diketones,  $\beta$  ketonic esters), the unstable enolates of mono C:O compds. have an increased reactivity, as shown, e. g., in their ability to add C:O compds. in the ketonic form. It was of interest to test, therefore, the reactivity of such enolates towards CO itself. To follow quant, the absorption of CO, an app. was constructed in which the ester enolates can be prep'd in N and then allowed to react with CO without admitting air. When  $\text{AcOEt}$ ,  $\text{PrCO}_2\text{Et}$ ,  $\text{PhCH}_2\text{CH}_2\text{CO}_2\text{Et}$  and  $(\text{PhCH}_2)_2\text{CHCO}_2\text{Et}$  are treated in  $\text{Et}_2\text{O}$  with powd. K, no gas is evolved; instead, the expected H is completely absorbed and a part of the ester enolate is converted into hydrogenated products. With  $\text{PhCH}_2\text{CO}_2\text{Et}$ , however, H is at once evolved (67.6% of the calcd. amt.), so that hydrogenation processes can have occurred to only a small extent and the "Et potassiumphenylacetate" (I) so prep'd must be much purer than the other ester enolates and better adapted for transformation reactions; it is also much less easily autoxidized than Et potassiumacetate. In its behavior towards CO, I does not differ from the purely aliphatic ester enolates. Freshly prep'd  $\text{Et}_2\text{O}$  emulsions absorb considerable dry CO on shaking, except those of the K deriv. of  $(\text{PhCH}_2)_2\text{CHCO}_2\text{Et}$  (probably because in this case the soln. contains no ester enolate but the "endiolate"  $(\text{PhCH}_2)_2\text{CHC(OK)C(OH)(CH}_2\text{Ph)}_2$ , formed by hydrogenation from 2 mols. of the former). With the metal derivs of the simple aliphatic esters, the products of the action with CO could be only incompletely sep'd. from those which had already been formed during the treatment of the ester with the alkali metal. With I, however, the isolation of the CO addn. product,  $\text{PhC(CHOH)CO}_2\text{Et}$ , is not interfered with by the  $\text{PhCH}_2\text{COCHPhCO}_2\text{Et}$  formed simultaneously by condensation of I with 1 mol. of non-enolized  $\text{PhCH}_2\text{CO}_2\text{Et}$ . The other ester enolates likewise form with CO  $\alpha$ -hydroxymethylene derivs of aliphatic esters, but as they closely resemble in chem. behavior the  $\alpha$ -ketonic esters which are always formed along with them, S and S attempted to prep. the Ac derivs from the K compds. and to sep. them by fractionation, with, however, only indifferent success. Addn. of CO was also detected with the enolates of ketones ( $\text{Me}_2\text{CO}$ ,  $\text{PhCOMe}$ ). It was hoped that the formation of hydrogenation products during the treatment of the esters with alkali metals, might be avoided by using  $\text{Ph}_3\text{CNa}$  ( $\text{Ph}_3\text{CNa} + \text{AcOEt} = \text{Ph}_3\text{CH} + \text{CH}_3\text{C(ONa)OEt}$ ), but while the purple  $\text{Et}_2\text{O}$  soln. of  $\text{Ph}_3\text{CNa}$  was immediately decolorized on adding  $\text{AcOEt}$ , it subsequently absorbed no CO on shaking. IV. Reaction of ester enolates with halogenalkyl and halogenacyl compounds. HELMUTH SCHEIBLER, ERICH MAHRENKEL AND DAVID BASSANOFF. *Ibid* 1198-204. An  $\text{Et}_2\text{O}$  soln. or suspension of "Et potassiumacetate," contg., besides  $\text{CH}_3\text{C(OK)OEt}$ , other condensation and hydrogenation products (cf. above), gives with  $\text{EtBr}$  a complex mixt. from which  $\text{PrCO}_2\text{Et}$  can be sep'd by fractional distn.  $\text{PhCHC(OK)OEt}$  similarly gives  $\text{PhCHEtCO}_2\text{Et}$ ; there is no O-substitution (formation of  $\text{PhCH:C(OEt)OEt}$ ). With  $\text{AcCl}$  instead of  $\text{EtBr}$ , however, both C- and O substitution occur, the products being  $\text{PhCHAcCO}_2\text{Et}$  (identified as the phenylhydrazone) and  $\text{PhCH:C(OAc)OEt}$  (hydrolyzed by cold 2.5% KOH to  $\text{PhCH}_2\text{CO}_2\text{H}$ ).  $\text{ClCO}_2\text{Et}$  yields exclusively the O product, phenylketene Et carboxyethyl acetal (I),  $\text{PhCH:C(OCO}_2\text{Et)OEt}$ , which with 1 equiv. of pure fresh alc. KOH decomps. in the cold into  $\text{PhCH}_2\text{CO}_2\text{Et}$  and  $\text{KO}_2\text{COEt}$ .  $b_p$  155-60°,  $d_{20}^{20}$  1.0970,  $d_4^{20}$  1.0950,  $n_D^{20}$  1.49366,  $n_D^{25}$  1.49766,  $1.50730$  for  $\alpha$ , D and  $\beta$  at 20°, instantly decolorizes Br in  $\text{CCl}_4$  and  $\text{KMnO}_4$  in  $\text{Na}_2\text{CO}_3$ . Attempts to reduce I to a deriv. of  $\text{PhCH}_2\text{CHO}$  led either to hydrolysis or to rearrangement. C. A. R.

Rearrangement of O-acyl into C-acyl compounds under the influence of noble-metal catalysts. I. HELMUTH SCHEIBLER. *Ber*, 58B, 1205-8(1925).—In an attempt to convert  $\text{PhCH:C(OCO}_2\text{Et)OEt}$  (I) (cf. preceding abstr.) into a deriv. of  $\text{PhCH}_2\text{CHO}$  by catalytic hydrogenation with Pt sponge, it was found that very little H was absorbed and the reaction mixt. on distn. yielded, besides  $\text{PhCH}_2\text{CO}_2\text{Et}$ , esters of  $\text{PhCH(CO}_2\text{Et)}$ .

Palladinized charcoal gives the same results, and the presence of H is not necessary; the rearrangement occurs just as well if the shaking app. is previously evacuated with a water pump. Possibly the I first attaches itself to the surface of the catalyst and thereby undergoes an activation which results in a loosening of the mol. structure; this probably occurs at the most sensitive part of the mol. (as shown by the behavior towards alc. KOH), and the resulting unstable energy-rich "enol ion,"  $\text{PhCH}:\text{C}(\text{OEt})\text{O} \dots$ , tends to assume the more stable ketone structure, the  $\text{CO}_2\text{Et}$  residue at the same time migrating to that C atom at which an excess of affinity is present.  $\text{PhCH}:\text{C}(\text{OEt})\text{O} \dots$

$\text{O} \dots \text{CO}_2\text{Et} \rightarrow \text{PhCH}(\text{CO}_2\text{Et})\text{C}(\text{OEt})\text{O}$  Neither in  $\text{Et}_2\text{O}$  at room temp. nor at  $100^\circ$  without a solvent could  $\text{PhOCO}_2\text{Et}$  be rearranged into  $\text{HOC}_6\text{H}_4\text{CO}_2\text{Et}$  by shaking with Pt sponge.

C. A. R.

Reaction of organomagnesium compounds on nitriles. *o*-Tolunitrile. M. JASPER. *Bull. soc. chim. Belg.* 34, 182-7 (1925).—Under normal reaction conditions *o*- $\text{MeC}_6\text{H}_4\text{CN}$  gives the following yields and products with various  $\text{RMgBr}$  compds.  $\text{EtMgBr}$ : 9% of ketone and 19% of *o*- $\text{MeC}_6\text{H}_4\text{C}(\text{NH})\text{Et}$ ,  $b_p$   $105^\circ$ ; HCl salt, m.  $175-7^\circ$ .  $\text{MeMgBr}$ : 20% ketone and 35% of *o*- $\text{MeC}_6\text{H}_4\text{C}(\text{NH})\text{Me}$ ,  $b_p$   $95^\circ$ ,  $d_{20}$  0.959, HCl salt m.  $183-5^\circ$ .  $\text{PhCH}_2\text{MgBr}$ : no isolatable ketone, 87% of *o*- $\text{MeC}_6\text{H}_4\text{C}(\text{NH})\text{CH}_2\text{Ph}$ ,  $b_p$   $185^\circ$ ; HCl salt, m.  $230-3^\circ$ .  $\text{PhMgBr}$ : no isolatable ketone, 85% of *o*- $\text{MeC}_6\text{H}_4\text{C}(\text{NH})\text{Ph}$ ,  $b_p$   $165^\circ$ ,  $d_{20}$  1.073; HCl salt, m.  $215-8^\circ$ .

WM. B. PLUMMER

Halogen compounds of tyrosine. R. ZEVNEK. *Z. physiol. Chem.* 144, 246-54 (1925).—Although tyrosine in neutral or alk. soln. gives humin substances when treated with Cl or Br, in acid soln. halogenation occurs without the formation of humins. The best yields are obtained by halogenation in AcOH. Chlorotyrosine (I), m.  $256-7^\circ$ ,  $[\alpha]_D^{20} -8.6^\circ$  in 4%  $\text{H}_2\text{O}$ ,  $-3.1^\circ$  in 4% HCl, was prepd. in 81-7% yield as the HCl salt by treating tyrosine in glacial AcOH with  $\text{SO}_2\text{Cl}_2$ , and from this the free base was obtained in 90-5% yield. It crystals with 1 mol.  $\text{H}_2\text{O}$ . In the cold the Mülton and Nasse reactions are negative;  $\text{FeCl}_3$  gives a violet color which becomes red on warming. Conc'd.  $\text{H}_2\text{SO}_4$  at  $100^\circ$  splits off HCl. *Base deriv.*, m.  $195^\circ$ . *Formyl deriv.*, m.  $193^\circ$ . Chlorobromotyrosine, m.  $252-4^\circ$ , from I and Br in AcOH. Chloronitrotirosine, m.  $208-10^\circ$ , from I and  $\text{HNO}_3$  in AcOH, but not from nitrotyrosine and Cl. Chloro *p*-hydroxyphenylethylamine-HCl, m.  $210^\circ$  (decompn.), from *p*- $\text{HOC}_6\text{H}_4\text{CH}_2\text{NH}_2$  and  $\text{SO}_2\text{Cl}_2$  in AcOH; free base, m.  $125^\circ$ . Bromotyrosine (II), m.  $246-9^\circ$  (decompn.),  $[\alpha]_D^{20}$  in 5%  $\text{H}_2\text{O} -7.0^\circ$ , in 4% HCl  $-3.7^\circ$ , from tyrosine and Br in  $\text{CH}_2\text{O}_2$ . It could not be obtained by treatment of tyrosine with Br and  $\text{SO}_2$  in AcOH, which gave the di-Br deriv., or by treatment of tyrosine in HBr-AcOH with  $\text{SO}_2\text{Cl}_2$ . Two cryst. forms were obtained with 1 and 2 mols.  $\text{H}_2\text{O}$ , resp., according to the temp. of crystn. Nitrobromotyrosine, m.  $204-8^\circ$  (decompn.), by treatment of II with  $\text{HNO}_3$  in AcOH and sepn. as the  $\text{HNO}_3$  salt, or in better yield as the HBr salt by treatment of nitrotyrosine in AcOH with excess of Br. Nitrotyrosine can thus be brominated but not chlorinated.

A. W. DOX

Condensation of phenylacetylene under the influence of primary amines. K. KRASOVSKII AND A. KIPRIANOV. *J. Russ. Phys.-Chem. Soc.* 56, 1-10 (1923).—The article is devoted to the study of the products of the reaction of  $\text{PhC}:\text{CH}$  with primary, secondary and tertiary amines. Under the influence of primary amines it condenses into the sym.  $\text{C}_6\text{H}_5\text{Ph}_2$ . Secondary and tertiary amines do not have this effect on  $\text{PhC}:\text{CH}$ .  $\text{PhC}:\text{CH}$  and 5 mols of an aq. 33% soln. of the amine ( $\text{MeNH}_2$  or  $\text{EtNH}_2$ ) were heated at  $250-66^\circ$  for 5-6 hrs. in sealed tubes. On cooling the tubes a cryst. mass of  $\text{C}_6\text{H}_5\text{Ph}_2$ , m.  $169-70^\circ$ , was obtained. With  $\text{EtNH}_2$  the yield is quant. On heating  $\text{PhC}:\text{CH}$  with  $\text{Me}_2\text{NH}$ ,  $\text{Et}_3\text{NH}$ , piperidine or  $\text{Me}_3\text{N}$  no crystals were obtained, but the  $\text{PhC}:\text{CH}$  was thickened into a butter-like substance. On heating  $\text{PhC}:\text{CH}$  in the same way with  $\text{NH}_3$ , KOH or water a brown tar was formed.

B. NELSON

Ethyl ester of  $\alpha$ -phenyl-*p*-nitrocinnamic acid. F. RANFALDI. *Atti accad. Lincei* (vi), 1, 38-42 (1923).—This ester forms prismatic mono-clinic crystals,  $a:b:c = 1.82871:1:0.91775$ ,  $\beta = 69^\circ 29'$ , which differ appreciably from those of the corresponding Me ester, m.  $141-142^\circ$  (cf. Scacchi, *Gazz. chim. ital.* 25, i, 310 (1895)).

B. C. A.

Isomeric rearrangements. II. Isomerization of rings. S. S. NAMEYKIN. *J. Russ. Phys.-Chem. Soc.* 55, 493-513 (1924).—A theoretical discussion of the exptl. results obtained by N. and collaborators (cf. *J. Russ. Phys.-Chem. Soc.* 46, 58 (1914); C. A. 18, 1487, 2885). Werner's idea of oscillating ring systems permits of a far better interpretation of the transformations of ring systems to those with more or fewer members than Baeyer's theory of tension is able to do. The min. force exerted by simple bonds in 3-, 4- and 5-membered rings is calcd. Stability of any alicyclic system is a function of a series of different factors. III. Dehydration of 1,2-dimethylcyclohexane-1,2-diol.

NAMETKIN AND DELECTORSKA. *Ibid* 514-20; cf. C. A. 18, 2885—IV. An irregular hydration of pinene oxide. S. S. NAMETKIN AND A. G. YARTZEVA. *Ibid* 521-4.—Prep'd from pinene nitrosobichloride and EtNHPh in alc. (cf. C. A. 18, 2511) optically inactive pinene (I) ( $b_D^{20}$  51-2°,  $n_D^{20}$  1.4662,  $d_4^{20}$  0.8593) and adding 8.5 g. of I to  $BzO_2H$  in  $Et_2O$  at 0° gives pinene oxide (II),  $b_D^{20}$  85-85.5°,  $d_4^{20}$  0.9647,  $n_D^{20}$  1.4688, after 5 days at room temp. Heating 7 g. II with 10 cc.  $H_2O$  in a sealed tube at 108-10° (2 hrs) and at 116-8° (3 hrs) produced two layers. The  $Et_2O$  exts. of the  $H_2O$  layer (satd. with  $K_2CO_3$ ) were united with the upper oil layer. After distg. off the  $Et_2O$  some crystals were obtained from the residue. After removing the adherent oil with unglazed tile and crystg.  $C_6H_6 + Et_2O$  the crystals m. 129.5-30° and were identical with inactive sobrerol, analogous to Prilezhaev's results with the active form (cf. C. A. 4, 916). Extn. of the unglazed tile gave pinol. The mechanism is probably: pinene  $\rightarrow$  pinene peroxide (cf. Engler, *Ber.* 31, 3046). The latter being unstable in  $H_2O$  is changed to pinene oxide  $\rightarrow$  sobrerol mixed with pinol.

H. BERNHARD

Camphor series. IV. SHIGERU KOMATSU AND CHIKAU FUJIO *Mem. Coll. Sci. Kyoto Imp. Univ. Series 7A*, No. 6, 389-95(1924)—Pinene  $HCl$  (I) (1 g.) was heated with various catalysts (2 g.) in sealed tubes to 100° or 200° for varying lengths of time and the yields of camphene were det'd. At 100°,  $FeCl_3$ ,  $SbCl_3$  and  $PCl_5$  are most active, giving yields of 60-70%, 60-64% and 90%, resp., in an hour or less, but the yield diminishes with further heating.  $AlCl_3$  and  $MgCl_2$  gave 30-44% while  $Al_2O_3$  and  $BaCl_2$  gave 14-20% yields. At 200°,  $Al_2O_3$  and  $AlCl_3$  gave 30-56%,  $MgCl_2$  21-31%,  $FeCl_3$  18-28%,  $SbCl_3$  11-18%,  $BaCl_2$  and  $PCl_5$  0%. Bornyl chloride (II) gave yields of 2-6% at 100°, 0% at 200° with  $FeCl_3$ . The yield diminishes with longer heating because of the formation of isobornyl chloride by addn. of  $HCl$  to camphene, and the formation of dipolymers. 25 g. of I heated with 25 g.  $FeCl_3$  in a sealed tube for an hour at 100°, the product steam distd., and the residue ext'd with  $Et_2O$  gave 1.2 g. of an oil  $b_D^{20}$  208-10°,  $n_D^{20}$  1.5304,  $d_4^{20}$  0.9649, mol. wt. 283, having a compn. nearly that of  $C_{15}H_{24}$ . With colloidal Pt the substance absorbed 2H. 50 g. of I was refluxed with 10 g.  $FeCl_3$  at 210-15° for 1.5 hrs., the product distd., and the 150-64° fraction redistd. over Na. Yield, 25 g. The substance was liquid and had a compn. intermediate between  $C_{15}H_{24}$  and  $C_{15}H_{12}$ . If I and  $FeCl_3$  were heated at 125-35°, a mixt. of about 20% liquid and 80% of the solid was obtained (Camphene), cf. C. A. 17, 1456, and *Ber.* 25, 147, 160(1892). The d.,  $n$  and elementary compns. of the various fractions were det'd. but no final conclusions reached.

M. A. YOUTZ

Camphylpropionic acid and trimethylenecamphane oxide. H. RUPF AND E. TSCHEPP *Helvetica Chim. Acta* 8, 351-7(1925)—While methylencamphylacetic acid (I) is not catalytically reduced as the free acid or the Na salt, the ester gives  $Et \beta$ -camphylpropionate (II),  $b_D^{20}$  169-70°, free acid,  $b_D^{20}$  198-9°, m. 63-4°; chloride,  $b_D^{20}$  142-4°; amide, m. 97-8°. If further reduced by Na and  $EtOH$  to trimethylenebornylglycol,  $b_D^{20}$  176-7°, m. 78° (47% yield), and bornyl- $\beta$ -propionic acid (III), m. 82-3°. Attempts to reduce the Et ester of I with Na and  $EtOH$  gave poor yields of the glycol. I adds  $HBr$ , giving the acid,  $C_{15}H_{22}O_3Br$ , m. 112° (decompn.). III and 10%  $H_2SO_4$  give the  $\delta$  lactone,  $b_D^{20}$  167°, which in I expt., was sapon'd. by  $NaOH$  to an isomeric III, m. 112-3°. The glycol and  $PBr_3$  give the bromohydrin,  $b_D^{20}$  142-4°, which yields, with  $MeOH-KOH$ , trimethylenecamphane oxide,  $b_D^{20}$  110-2°,  $d_4^{20}$  0.9709,  $n_D^{20}$  1.48140, 1.48386, 1.48881 for  $\alpha$ , D and  $\beta$ ,  $[\alpha]_D^{20}$  -0.58, -0.59, -0.63 and -0.73° for C, D, Hg and F.  $HBr$  gives an oil,  $C_{15}H_{22}O_3Br$ ,  $b_D^{20}$  144-6°, which, however, is probably not the bromohydrin mentioned above.

C. J. WZST

Conversion of cholesterol into 4-hydroxycholestanic acid. A. WINDAU AND R. HOSSFELD. *Z. physiol. Chem.* 145, 177-83(1925)—The prep'n. of 4-chlorocholestanic acid (I) from cholesteryl chloride can be greatly shortened by the use of Pt catalyst in the hydrogenation and a mixt. of  $Et_2O$  and  $AcOH$  as the solvent. Oxidation of I in  $AcOH$  by  $CrO_3$  gave 4-chlorocholestanic acid (II), m. 175-6°. Me ester, m. 128°, by esterification with  $CH_3N_3$ . Treatment of II with  $Cu(OAc)_2$  and 5%  $KOH$  6 hrs. at 160-70° gave 4-hydroxycholestanic acid (III), m. 208°; Me ester, m. 162°. Oxidation of III gave the tri- $CO_2H$  acid,  $C_{27}H_{44}O_6$ , isomeric with isolithobianic acid. By oxidation of the di-Ac deriv. of 4-hydroxy-7-oxocholestanic acid with  $CrO_3$ , a lactone acid,  $C_{27}H_{44}O_6$ , m. 195-6°, was obtained, which was monobasic in cold and dibasic in hot solns. Me ester, m. 99°.

A. W. DOX

Dehydrogenation of cholesterol (preliminary communication). OTTO DIELS AND WILLY GÄNKE. *Ber.* 58B, 1231-3(1925)—When cholesterol is heated a long time in a quartz vessel with "active" charcoal impregnated with 5-10% Pd,  $H_2O$  is first set free, then the 8-C-atom side chain is split off as isooctane or isooctylene ( $C_{11}H_{22}$  is also

probably split off) and among the high boiling reaction products is obtained a cryst. substance resembling anthracene in appearance and in the fluorescence it imparts to its solns. but having a compn and mol wt in camphor (217-43) corresponding to anthracene-indene,  $C_{13}H_{14}$  C. A. R.

**Benzylbenzoin (benzoylphenylbenzylcarbinol).** J. PASCUAL VILA AND J. CEREZO. *Anal. soc. españ. fis. quim.* 23, 7b-8 (1925).—It is now considered that the original formula assigned to benzylbenzoin (Garcia Banus and Pascual Vila, C. A. 16, 3179) is correct and that it is not the benzyl ether of benzoin as suggested in a more recent communication (C. A. 19, 59). The prepn of benzylbenzoin by the action of  $PhCl_2Cl$  on the product of the reaction of benzoin with  $K_2Hg$  is described. B. C. A.

**Beckman rearrangement. V. Oximes of *p*-methoxybenzyl.** JACOB MEISENHEIMER, HANS LANGE AND WALTER LANFARTER. *Ann.* 444, 94-112 (1925), cf. C. A. 18, 2154.—According to the Hantzsch Werner theory, unsym. substituted benzyls should yield 4 mono- and 4 dioximes. This is shown to be true of *p*-methoxybenzyl. 4'-Methoxy-7'-nitrostilbene (1 g.) and 10 cc. 30% MeOH KOH are gradually heated to 150°, giving 70-80% of  $\alpha$ -4'-methoxybenzyl 7'-oxime 7,7-dimethylacetal ( $\alpha$ -acetalo-xime) (I), m. 205°, which, warmed with 4 parts AcOH at 100° gives a quant. yield of  $\alpha$ -4'-methoxybenzyl-7'-oxime ( $\alpha$ -monoxime) (II), m. 108-10°, boiling it with EtOH transforms it into the  $\beta$ -deriv. as does 24 hrs. standing in concd. HCl. It does not yield cryst. acyl derivs. with  $Ac_2O$  or with  $BzCl$  in  $C_6H_5N$ . The  $\beta$ -monoxime, m. 170°, results in quant. yield from I and concd. HCl at room temp. for 15-20 hrs.; *Ac* deriv., m. 99-100°, II, or the  $\alpha$ -deriv., in 15% NaOH, gives with  $NH_4OH$  HCl 75-80% of  $\alpha$ -*p*-methoxybenzyl dioxime (III), m. 206-7°; the reaction also takes place equally well in acid EtOH soln. *Di-Ac* deriv., m. 108°.  $\beta$ -Deriv., m. 176°, results in 10% yield by boiling III in EtOH for 30 hrs.; 12 hrs. in a sealed tube at 150° gives a quant. yield, as does warming with moderately concd. NaOH at 100° for 5-6 hrs. *Di-Ac* deriv., m. 130°. The  $\beta$ -monoxime and  $NH_4OH$  HCl in 15% NaOH at 50-60° gives the  $\gamma$ -dioxime, m. 89-91°; it is slowly transformed into the  $\beta$ -deriv. in  $C_6H_5N$ , quickly in EtOH and  $Et_2O$ , also by warming an aq. alk. soln. or by heating above its m. p. *Di-Ac* deriv., m. 100-2°; this is as labile as the free oxime. With excess concd. NaOH at room temp. there results phenylanisylfuran (IV), m. 80°. The  $\beta$ -oxime and  $NH_4OH$  HCl in 10% NaOH at room temp. for 24 hrs. gives the  $\delta$ -dioxime, m. 114-5°, crystg. with 0.5 mol.  $C_6H_5N$ ; heated at 15 mm. to 155°, there sublimes unchanged  $\delta$ -dioxime, IV and  $\beta$ -dioxime. EtOH or alkali as well as heating above the m. p. transforms it into the  $\beta$ -deriv. Acetylation at 0° gave a product that crystd. poorly and on sapon gave a mixt. of 67% IV and 23%  $\alpha$ -dioxime; at other temps. other ratios were obtained, the % of anhydride decreasing with increasing temp. Oxidation of the  $\gamma$ -dioxime with NaOCl gives a quant. yield of  $\alpha$ -phenylanisylfuroxan, m. 106-7°; the  $\delta$ -dioxime gives the  $\beta$ -deriv., m. 95-7°. The  $\alpha$ - or  $\beta$ -deriv., on oxidation, gives a mixt. of these 2 products, whose sepn. is difficult. Reduction gives the  $\gamma$ - or  $\delta$ -dioxime, from which they were prepd. C. J. WEST

**$\beta$ -Methylnaphthalene derivatives. I.** KAROL DZIEWONSKI, JADWIGA SCHOENOWNA AND EMIL WALDMANN. *Ber.* 58B, 1211-8 (1925).—2-Methylnaphthalene 6-sulfonic acid (I) is obtained in about 80% yield (as the Ba salt) by heating 10 g. 2- $C_{10}H_7Me$  and 7.5 cc.  $H_2SO_4$  (d. 1.84) 5-6 hrs. at 90-100°, dilg. with  $H_2O$ , neutralizing with  $BaCO_3$  and filtering from the  $BaSO_4$ ; Na salt. Chloride, from the Na salt and  $PCl_5$ , m. 97-8°. Amide, m. 205-6°; easily sol. in alkalies. Et ester, from the chloride in boiling alc., m. 79-80°. 2-Methyl-6-hydroxynaphthalene (II), from the Na salt of I fused with KOH at 280-300°, m. 128-9°, gives no color with bleaching powder, becomes olive-green when heated with  $FeCl_3$ , and first dark blue, then green, with  $CHCl_3$  and KOH; *Me* ether, leaflets of characteristic pleasant odor, m. 78-9°; benzoate, m. 128-9°; 5-NO deriv., from II and  $ZnCl_2$  in alc. treated with aq.  $NaNO_2$ , orange-yellow, m. 119-20°, sol. in cold concd.  $H_2SO_4$  with brown-red color and repptd. unchanged by  $H_2O$ , forms green alkali salts, is oxidized by  $HNO_3$  (d. 1.25) in an equal vol. of  $H_2O$  to the 5- $NO_2$  compd., lemon-yellow needles, m. 81-2°, sol. in dil. NaOH with blood-red color; 5- $NH_2$  compd., from the Ba salt of the NO deriv. in 1%  $NH_4OH$  suspension with  $H_2S$ , m. 155-7°, easily sol. in dil. mineral acids, easily alters in the air in the basic form (especially in the presence of alkalies), becoming brown, is converted in dil. soln. by  $H_2SO_4$   $K_2Cr_2O_7$  into 2-methyl-5,6-naphthoquinone, orange-yellow, m. 131-2°. 5-Azo deriv. of II: Benzene, from II in NaOH- $Na_2CO_3$  and  $PhN_2Cl$ , red, m. 135-6°, almost insol. in alkalies, easily sol. in concd.  $H_2SO_4$  with fuchsin-red color; *p*-nitrobenzene, dark red leaflets with green metallic luster, m. 244-5° (both of these azo dyes can, like para-red, be produced on cotton fibers from their constituents and yield brilliant red, soap-fast colors); *p*-sulfobenzene, is obtained as the Na salt, red needles with golden luster, dyes animal

fibers in an acid bath a brilliant red. **2-Methylaminonaphthalene**, from  $\text{II}(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{OH}$  at  $150^\circ$  in sealed tubes, m.  $129-30^\circ$ , easily sol. in mineral acids, becomes pink after a time in the air. *Ac deriv.*, m.  $155-6^\circ$ , oxidized in boiling  $\text{H}_2\text{O}$  in the presence of  $\text{MgSO}_4$  by  $\text{KMnO}_4$  to **6-acetamino-2-naphthoic acid**, m.  $271-2^\circ$ , which is hydrolyzed by boiling  $\text{HCl}$  to the free  $\text{NH}_2$  acid, m.  $222-3^\circ$ , easily sol. in dil. mineral acids, shows both feebly basic and feebly acid properties. C. A. R.

**Catalytic action.** VIII. Catalytic reduction of  $\beta$ -naphthylamine. TOROBU HARA. *Mem. Coll. Sci. Kyoto Imp. Univ. Series 7A*, No. 6, 403-7 (1924); cf. C. A. 17, 2577—Fifty-four g. of  $\beta\text{-NH}_2\text{C}_{10}\text{H}_7$  was passed with  $\text{H}$  over  $\text{Ni}$ , prepd. by reduction, during 200 hrs. Among the products were identified  $\text{NH}_4$  tetrahydronaphthalene, dihydronaphthalene (traces),  $\text{C}_{10}\text{H}_8$  (traces),  $\beta$ -ar tetrahydronaphthylamine (18.8 g.),  $\beta, \beta$ -di-ar tetrahydronaphthylamine (17 g.). The hydrocarbons amounted to 11.3 g. A total of 74% of the amine formed ar- and 26%, ac-compds. M. A. Yourtz.

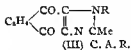
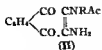
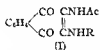
**Migration of the  $\alpha$ -naphthyl radical.** E. LUCE. *Compt. rend.* 180, 145-8 (1925)—No migration of a radical occurs when  $\text{AgNO}_3$  or  $\text{HgO}$  reacts with the iodohydrins of  $\alpha$ -phenyl  $\alpha$ -naphthylethylene (Acres, *Ber.* 37, 2753-64 (1904)) and of  $\alpha$ -phenyl- $\alpha$ -naphthylpropylene,  $\text{CPh}(\text{C}_{10}\text{H}_7)\cdot\text{CHMe}$  (m.  $55-61^\circ$ , b<sub>25</sub>  $232-6^\circ$ ), the reagents merely removing the elements of  $\text{HIO}$ .  $\beta$ -Hydroxy- $\beta$ -phenyl- $\beta$ -1-naphthylethylamine,  $\text{C}_{10}\text{H}_7\cdot\text{CPh}(\text{OH})\text{CH}_2\text{NH}_2$ , m.  $161^\circ$  [ $\text{HCl}$  salt, m.  $244^\circ$  (decompu)], chloroplatinate, decompu. above  $187^\circ$ , from  $\alpha\text{-C}_{10}\text{H}_7\text{MgBr}$  and  $\text{PhCOCH}_2\text{NH}_2$ ,  $\text{HCl}$  is converted by  $\text{HNO}_3$  (cf. McKenzie and Roger, C. A. 18, 2153) into  $\alpha$ -phenyl- $\alpha$ -naphthylmethyl ketone, m.  $56.5-57^\circ$  (oxime, m.  $143-151^\circ$ ). The constitution of this substance follows from the synthesis of the other possible product (which would result if the  $\text{Ph}$  radical migrated instead of the  $\text{C}_{10}\text{H}_7$ ), viz.,  $\alpha$ -naphthyl benzyl ketone, m.  $64.5-65^\circ$ , prepd. from  $\text{PhCH}_2\text{COCl}$  and  $\text{C}_{10}\text{H}_7\text{MgBr}$ , and also by oxidation of the product of interaction of  $\alpha\text{-C}_{10}\text{H}_7\text{MgBr}$  and  $\text{PhCH}_2\text{COCl}$ .  $\beta$ -Naphthyl benzyl ketone, m.  $99.5^\circ$  (picrate), is also produced in the above Friedel and Crafts reaction. The compd. previously described by Graebe and Bungener (*Ber.* 12, 1078-9 (1879)) as  $\alpha$ -naphthyl benzyl ketone, m.  $57^\circ$ , was a mixt. of the  $\alpha$ - and  $\beta$ -isomerides. B. C. A.

**Derivative of 2,3-diamino-1,4-naphthoquinone.** K. FREES AND K. BILLIG. *Ber.* 56B, 1128-38 (1925)—Just as acylation of the  $\text{NH}_2$  group in 2-amino-3-chloro-1,4-naphthoquinone renders the  $\text{Cl}$  atom reactive (C. A. 17, 3334), so after acylation of the 2-aryl- and alkylamino derivs. the  $\text{Cl}$  reacts easily with  $\text{NH}_3$ , amines and alcoholates; the most varied derivs. of 2,3-diamino-1,4-naphthoquinone, for which there was hitherto no method of prepn., are thus rendered readily available. Attempts to obtain the free amines from the  $\text{Ac}$  derivs. of type I and II failed as a result of the pronounced tendency of such compds. to lose  $\text{H}_2\text{O}$ , both with acids and bases, with formation of imidazole quinones (III). If, however, inorg. acid derivs. are used instead of the  $\text{Ac}$  derivs., the free amines can readily be obtained. For this purpose the  $\text{N-NO}$  derivs. proved to be especially useful because of the ease with which they are prepd. and of their great reactivity. With  $\text{NH}_3$  and amines they often exchange the  $\text{Cl}$  for  $\text{NHR}$  more easily than the  $\text{Ac}$  derivs. With alkalis they behave differently from the  $\text{Ac}$  derivs.; thus, while with 2-acetylanilino-3-chloro-1,4-naphthoquinone (IV) the hydrolysis is more rapid than the exchange of  $\text{Cl}$  for  $\text{HO}$ , with the 2- $\text{PhN}(\text{NO})$  deriv. (V) the opposite is true. 2,3-

**Dianilino-1,4-naphthoquinone** (VI) has the grouping  $-\text{CO}\cdot\text{C}(\text{NH})\cdot\text{C}(\text{NH})\cdot\text{CO}-$  in common with indigo and resembles indigo in many of its properties (blue color in the solid state, dark red color in the vapor state, tendency to dissolve in different solvents with widely varying shades, lack of tinctorial power of its orange-yellow di- $\text{Ac}$  deriv.); as a vat dye, however, VI is far inferior to indigo (about 25 times weaker and dyeing wool only in a strongly alk. vat at about  $50^\circ$ ). As stable as the aryl derivs. of I are to alkalis and dil. acids, they are very little resistant to concd.  $\text{H}_2\text{SO}_4$ ; 2-amino-3-anilino-1,4-naphthoquinone (VII) is completely converted into the 2- $\text{HO}$  deriv. and VI yields a compd. (VIII) believed to be phenylbis-[2-anilino-1,4-naphthoquinone-3-amine. 2-Acetamido-3-anilino-1,4-naphthoquinone, from the 3- $\text{Cl}$  deriv. and  $\text{PhNH}_2$  in boiling alc. (yield, 80%), deep red crystals with the color, luster and form of  $\text{KMnO}_4$ , m.  $200^\circ$ , pptd. unchanged by acids from the fresh blue-violet solns. in cold alc. alkalis, but on longer standing or warming there is formed 2-methyl-2-phenyl-2-anilino-naphthimidazole 4,9-quinone (IX), which also results on fusion or heating with alc.  $\text{NH}_3$  or strong acids and in boiling  $\text{AcOH}$  with  $\text{NaNO}_2$  (at room temp. there is first formed with  $\text{NaNO}_2$  2-acetamido-3-N-nitrosoanilino-1,4-naphthoquinone, yellow, m.  $129^\circ$ ). IV, from the 2- $\text{PhNH}$  deriv.  $\text{Ac-O}$  and concd.  $\text{H}_2\text{SO}_4$ , yellow, m.  $135^\circ$ , gives in  $\text{C}_6\text{H}_6$  with dry  $\text{NH}_3$  50-60% of the 3- $\text{NH}_2$  deriv., yellow, m.  $167^\circ$ , which is converted by acids and alkalis into IX; 3- $\text{PhNH}$  deriv., from IV and  $\text{PhNH}_2$  in hot alc., bright red, m.  $157^\circ$ , sol. in alc.

KOH with red-violet color and hydrolyzed to VI on short heating. IX, yellow, m. 239°, volatile without decompn., repptd. unchanged by H<sub>2</sub>O from the yellow-green soln. in concd. H<sub>2</sub>SO<sub>4</sub>, forms with alk. Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> an orange-yellow vat becoming dark green at first in the air and then lightening in color and depositing the IX. With Zn dust in hot EtOH IX gives 2-methyl-3-phenyl 4,9-dihydroxy *lm*-naphthimidazole, sinters 100°, m. 157° (decompn.), very sensitive to atm O, diacetate, m. 182°, hydrolyzed in the air directly to IX. 3-2'-Naphthyl analog of IX, yellow, m. 222° V (Plagemann, *Ber.* 16, 895(1883)), m. 126°, is obtained more conveniently than by P's method and in very good yield by slowly treating the 2 PhNH compd. in cold AcOH suspension with NaNH<sub>2</sub> until the original substance has dissolved and been replaced by the light yellow crystals of V; with arylamines either (1) it loses the NO group with regeneration of the original 2-PhNH compd., or (2) it exchanges the Cl for the RNH residue with formation of the 3-arylamino deriv. in which, however, the NO group is replaceable by H with the greatest ease. In which of these 2 ways the V will react predominantly depends on the conditions and especially on the nature of the arylamine. PhNH<sub>2</sub>, *p*-MeC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>, *p*-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>, and *p*-MeOC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> react almost quant. according to (2), *o*- and *m*-MeC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>, PhNHMe, PhNMe<sub>2</sub>, *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>, *p*-ClC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>, 2 C<sub>10</sub>H<sub>7</sub>NH<sub>2</sub> and PhNHNH<sub>2</sub> almost exclusively according to (1), and 1-C<sub>10</sub>H<sub>7</sub>NH<sub>2</sub> and *o*-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> according to both (1) and (2), (1) predominating. 2-N-Nitroso-*p*-toluidino 3-chloro 1,4-naphthoquinone, yellow, sinters and reddens around 115°, m. 140°; *p*-anisidino analog, orange, m. 177° (decompn.); *β*-naphthylamino compd., orange, blackens around 150°, m. about 180°. 3-Hydroxy-2-anilino-1,4-naphthoquinone, from V and hot alc. NaOH (Plagemann), from VII and concd. H<sub>2</sub>SO<sub>4</sub>, or from 2-amino or 2-anilino-3-N-nitroso-anilino-1,4-naphthoquinone and alc. NaOH, indigo blue, m. 212°. 2-2'-Naphthylamina analog, blue, m. 228°. 3-Amino-2-N-nitrosoanilino-1,4-naphthoquinone (X), yellow, sinters 138° and blackens, with formation of XI (below), is obtained, usually mixed with XI, from the 3-Cl deriv. in hot alc. with concd. NH<sub>4</sub>OH, owing to its instability it cannot be sepd. from XI by fractional crystn. but it can be obtained pure by slowly adding NaNO<sub>2</sub> to VII in cold AcOH until the blue-red soln. changes to orange-yellow; with hot alkalis it evolves NH<sub>3</sub> and the NH<sub>2</sub> group is replaced by HO and the NO group by H. VII, from X added to an excess of SnCl<sub>2</sub> in AcOH at room temp. and then treated with dil. FeCl<sub>3</sub>, indigo-blue, m. 197°, forms blue-violet to cherry red solns., yields with strong acids deep red salts which are very easily hydrolyzed; the red soln. in concd. H<sub>2</sub>SO<sub>4</sub> allowed to stand 24 hrs. and poured into H<sub>2</sub>O gives the 2-HO compd.; with Ac<sub>2</sub>O it gives the 2-NHAc deriv. (above). 1-Phenyl-*lm*-naphthotriazole 4,9-quinone (XI), obtained quant. from VII or X in boiling AcOH, pale greenish yellow leaflets with Ag luster, m. 241°, identical with the product obtained by Wolff from *α*-naphthoquinone and PhN, (C. A. 7, 3740). 1-*p*-Tolyl homolog, greenish yellow, m. 212°. 2-Anilino-3-N-nitrosoanilino-1,4-naphthoquinone, from 5 parts V and PhNH<sub>2</sub> at room temp., yellow-brown, m. about 165° (decompn.), decomps. in all solvents on heating, dissolves in alc. NaOH with red color and is repptd. unchanged by acids but if the soln. is heated acids now ppt. the 3-HO compd. (yield, 80% with 10 parts alc. and 1 part of 10% NaOH). VI, from V and 4 parts PhNH<sub>2</sub> on the H<sub>2</sub>O bath or by hydrolysis of IV, indigo-blue needles or rodlets from xylene, blue violet quadratic tables with beautiful surface luster from C<sub>6</sub>H<sub>5</sub>N or PhNO<sub>2</sub>; its cold solns. are usually deep blue (soft green in PhNH<sub>2</sub>) but hot solns. more frequently differ in color: paraffin, dark red; PhNO<sub>2</sub> and PhNH<sub>2</sub>, red-violet; C<sub>6</sub>H<sub>6</sub> and xylene, pure violet; C<sub>6</sub>H<sub>5</sub>N, bluish green; CHCl<sub>3</sub>, greenish blue. With Ac<sub>2</sub>O and AcCl it gives IV, with NaNO<sub>2</sub> in AcOH the mono-*N*-NO deriv., with much boiling Ac<sub>2</sub>O treated repeatedly with small amts. of AcCl the di-*Ac* deriv., yellow, becomes brown 240° and finally deflagrates. With Zn dust in hot Ac<sub>2</sub>O, VI yields 2,3-dianilino-1,4-diacetoxynaphthalene, m. 243° (decompn.), easily hydrolyzed by alc. NaOH to the di-HO compd. 2,3-Diacetanilido-1,4-diacetoxynaphthalene, from the di-*Ac* deriv. of VI with Zn dust in Ac<sub>2</sub>O, darkens 220°, deflagrates about 245°, hydrolyzed in the air directly to VI. VIII, from VI allowed to stand 24 hrs. in concd. H<sub>2</sub>SO<sub>4</sub>, corn flower-blue, m. 263°. 2-Anilino-3-*p*-toluidino-1,4-naphthoquinone, from 2-acetanilido- or N-nitrosoanilino-3-chloronaphthoquinone and *p*-MeC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> or from 2-acet-*p*-toluidino- or N-nitroso-*p*-toluidino-3-chloronaphthoquinone and PhNH<sub>2</sub>, black-green needles, m. 177°. 3-*p*-Anisidino analog, from acetanilido- or nitrosoanilinochloronaphthoquinone and *p*-MeOC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> (nitrosoanisidinochloronaphthoquinone and PhNH<sub>2</sub> give only anisidinochloronaphthoquinone), dark blue-green leaflets with strong surface luster, m. 180°. Other 2,3-derivs. of 1,4-naphthoquinone: *p*-toluidino-*p*-anisidino, dark green, m. 170°; *p*-toluidino-*m*-toluidino, dark green, m. 155°; di-*p*-toluidino, indigo-blue, m. 179°; anilino-*p*-aminoanilino, blue-black, m. 197°. Et 2-acetanilido-1,4-naphthoquinone-3-acetoacetate, from IV, AcCH<sub>2</sub>CO<sub>2</sub>Et and Na in cold abs. alc. (yield

70-80%), yellow, m. 160°, 2-NHAc analog (yield, 20%), yellow, m. 143°, slowly decomps in boiling AcOH, evolves  $\text{NH}_3$  with hot alc NaOH.



Catalytic reduction of cyano compounds. H RUPE AND F. GYSIGER *Helvetica Chim. Acta* 8, 338-51 (1925), cf. *C. A.* 18, 238, 255; 19, 825.—The reduction of  $\text{Ph}_2\text{CHCN}$  stops when 70-78% of the amt. of H calcd. for 2 mols. is absorbed; the reaction products consist of 30% of  $\alpha, \alpha$ -diphenylethylamine, b<sub>11</sub> 170°, m. 38° (cf. Freund and Immerwahr, *Ber.* 23, 2846 (1890)); it quickly absorbed  $\text{CO}_2$  from the air; chloroaurate, deep yellow; phenylthiourea, m. 171°; Ac deriv., m. 86°; Bz deriv., m. 123°; a very small amt. of sec  $\alpha, \alpha$ -diphenylethyl amine, isolated as the HCl salt, m. 159°, whose nitrosamine m. 179°, and some  $\text{Ph}_2\text{CHCN}$ .  $\text{Ph}_2\text{CHCN}$  is reduced very slowly and gives only triphenylethylamine, isolated as the HCl salt, m. 214°. Reduction of  $m\text{-NCCCH}_2\text{NHC}_6\text{H}_4\text{CO}_2\text{H}$ , either as the free acid or Na salt, gave a complicated mxt., from which a small amt. of a Ba salt of unknown constitution was isolated. The reduction of  $\text{PhNHC(CN)NPh}$  is likewise complicated and is accompanied by a rupture of the chain, since  $\text{PhNH}_2$  and HCN were the only products isolated.  $\text{BzCH}_2\text{CH(CN)Ph}$  yields a primary base which immediately splits off  $\text{H}_2\text{O}$ , yielding a diphenylpyrroline (I), b<sub>11</sub> 204-6°, b<sub>12</sub> 210-2°, m. 50°, somewhat volatile with steam; acid  $\text{KMnO}_4$  is quickly decolorized, alk  $\text{KMnO}_4$  more slowly; a pine stick moistened with HCl is turned violet by the base; it could not be further reduced nor does it yield a nitrosamine. *N*-Ac deriv., m. 105°; *N*-Bz deriv., m. 180°; picrate, yellow, m. 156°; acid oxalate, m. 157-8°. There also results a small amt. of an isomeric base, m. 176°, which gives a violet-red soln. in AcOH and a dark red soln. in  $\text{H}_2\text{SO}_4$ . Reduction of  $\text{BzCH}_2\text{CH(CN)Ph}$  in boiling EtOH-AcOEt gives a mxt. of I and diphenylpyrrolidine, b<sub>12</sub> 193-5°, sep'd by the insolv. of the acid oxalate, m. 230°, in EtOH; HCl salt, m. 154°; phenylthiourea, m. 188°.  $\text{BzCH(CN)Ph}$  is reduced to the aldimine of benzoylphenylacetaldehyde, m. 173°, and hydroxymethyldeoxybenzoin, m. 93° (Claisen and Mayerowitz, *Ber.* 22, 3278 (1889)), which with  $\text{PhNHNH}_2$  yields 1,4,5-triphenylpyrazole, m. 207°. C. J. WEST

Fungus dyestuffs. II. The dye of the blood-red "Hautkopf" (*Dermocybe sanguinea* Wulf.). FRITZ KOGL AND J. J. POSTOWSKY *Ann.* 444, 1-7 (1925); cf. *C. A.* 19, 639.—The fungus, *Dermocybe sanguinea* Wolf, was dried, ext'd with EtOH, the residue of the ext. treated with 3%  $\text{NH}_4\text{OH}$  and, after filtering, the dye pptd by acid. Adding 10 vols.  $\text{H}_2\text{O}$  to the  $\text{C}_{12}\text{H}_{11}\text{N}$  soln. ppts. emodin (3% yield of the dry powder); dil. HCl ppts. from the filtrate a new dye, *dermocybin*,  $\text{C}_{12}\text{H}_{11}\text{O}_7$  (I), red needles, m. 228-9°, sol in conc'd  $\text{H}_2\text{SO}_4$  with a deep violet, in alkali with a red-violet color; it dyes Cr-mordanted wool a violet-red. The spectra are given for conc'd and dil.  $\text{H}_2\text{SO}_4$  and 0.1 *N* NaOH. *Tetra-Ac deriv.*, yellow, m. 182°. Conc'd  $\text{H}_2\text{SO}_4$  splits off 1 Me group, giving a pentahydroxy- $\beta$ -methylanthraquinone, red, m. 289°; the soln. in conc'd.  $\text{H}_2\text{SO}_4$  and alkali have the same colors as I and dye wool the same color. The spectra in conc'd.  $\text{H}_2\text{SO}_4$  and in  $\text{Al}_2(\text{SO}_4)_3$  soln. are given. Distn. with Zn dust gives  $\beta$ -methylanthracene. I is therefore a pentahydroxymethoxy  $\beta$ -methylanthraquinone. C. J. WEST

Hystazarindiquinone or 2,3,9,10-anthradiquinone. MUNENARI TANAKA. *Chem. News* 131, 20-2 (1925).—A paste of hystazarin  $\text{C}_{12}\text{H}_9\text{N}$  salt and AcOH is oxidized with  $\text{Pb}(\text{OAc})_2$ , giving 5% of 2,3,9,10-anthradiquinone, red with a metallic luster, darkens above 315°, is stable in the air but is reduced by HI or  $\text{H}_2\text{SO}_4$ . C. J. WEST

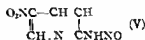
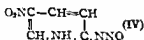
Action of iodine on desmotroposantonin: artemisic acid. P. BERTELO. *Atti accad. Lincei* [vi], 1, 127-30 (1925).—The action of I on desmotroposantonin in glacial AcOH yields an acid identical, except for a lower m. p., in every way with artemisic acid (cf. *C. A.* 18, 832). B. C. A.

The action of hydrazine on dimethylpyrone. N. KISHNER. *J. Russ. Phys. Chem. Soc.* 53, 539-45 (1924).—Powd. dimethylpyrone (I) (30 g.) admixed in small portions with 45 cc. 90%  $\text{N}_2\text{H}_4$ ,  $\text{H}_2\text{O}$  (II) gradually went in soln., evolving heat. The excess of II having been dist'd. off at 130° under 40 mm. a viscous, almost colorless liquid (III) remained in the flask;  $\text{N}_2$  analysis suggests  $\text{C}_{12}\text{H}_{12}\text{N}_4$  (—1% off). III is sol in  $\text{H}_2\text{O}$ ; aq. HCl splits off  $\text{N}_2\text{H}_4$ . Brought to 240° under 10 mm. III becomes a faint yellow glass-like mass ( $\text{C}_{12}\text{H}_{12}\text{N}_4$ ), which when heated, to beginning decompn. continues giving off  $\text{NH}_3$  and  $\text{N}_2$ , apparently 2 simultaneous reactions taking place. The reddish brown, solidified residue, purified by vacuum distn., forms a hard, bright yellow mass,  $\text{C}_{12}\text{H}_{12}\text{N}_4$  (IV), m. 251°. IV easily takes up liquids of crystn., EtOH being again given

off in the air; IV. MeOH m. 254°; IV. 4AcOH m. 73°; IV. 4HCl, exists in soln only. IV and excess of MeI heated at 100° 3 hrs in a sealed tube gave a product  $C_{11}H_{11}N_4$ , MeI, needles from MeOH.

H. BERNHARD

Some reactions of 2-nitramino-5-nitropyridine. C. RÄTH AND G. PRANGE *Ber* 58B, 1208-10(1923); cf. Chichibabin and Menshikov, *C. A.* 19, 1863—2,5- $C_4H_2N$ -( $NHNO_2$ ) $NO_2$  (I) heated in alk. soln. soon begins to give off  $N_2O$  vigorously, with spontaneous evolution of heat, and yields quant. the light yellow Na salt of 2,5- $C_4H_2N$ -(OH)- $NH_2$  (II), pure white, m. 191-2° (described in the literature as being faintly yellow and m. 184°). With Zn dust in cold alk. soln., however, I gives a yellow-gray ppt. converted by HCl into a light yellow powder (III) which, from its compn. and behavior, probably has the structure IV or V. Much more energetic reduction with Zn and concd. HCl gives 2,5- $C_4H_2N$ -( $NH_2$ ) $_2$ . Chichibabin says that with concd.  $H_2SO_4$  under suitable conditions I rearranges into 2,3,5- $C_4H_2N$ -( $NH_2$ ) $(NO_2)_2$ , repetition of his work showed that there is indeed obtained a compd. m. 192° but that it is II. The Na salt of II seps, with  $3H_2O$  and deflagrates about 303°. 2-Nitrosamino-5-nitropyridine (III), deflagrates about 240°, sol. in hot concd. HCl and reprecipitated by  $H_2O$ , detonates violently when moistened with concd.  $H_2SO_4$  or when heated in a tube.



C. A. R.

Synthesis of the carboxylated cryptopyrrolecarboxylic acid and of some methenes, also a contribution to Ehrlich's dimethylaminobenzaldehyde reaction. HANS FISCHER AND COSTIN NENTRESCU. *Z. physiol. Chem.* 145, 295-307(1925).—The color reaction obtained by condensing pyrrole derivs. with  $p-Me_2NC_6H_4CHO$  in the presence of HCl has been attributed to the formation of dipyrrolylphenylmethane dyes. Where such products were identified, however, the reaction cannot be considered strictly analogous to the formation of Ph<sub>2</sub>CH dyes for the reason that higher temps. and non-aq. solvents were employed. By the use of  $HClO_4$  instead of HCl for the condensing agent, crystalline products have now been obtained which are shown to be pyrrylphenylmethane derivs. 2,4-Dimethyl-3-[di-β-carboxy]ethyl-5-carboxypyrrole, m. 85-90° (decompn.), was prepd. by sapon. of its ester. By heating the tri-Na salt with excess of  $CH_3O_2$  and  $HClO_4$ , bis-[2,4-dimethyl-3-dicarboxyethyl]-5-methene crystd. out as the yellow  $HClO_4$  salt. The  $HCl$  salt of the tetra-Me ester m. 218° and is easily saponified by 10% NaOH into the tetra-Na salt. Treatment of the acid or its Na salt with  $p-Me_2NC_6H_4CHO$  and 10% HCl gave  $p$ -dimethylaminophenyl-2,4-dimethyl-3-dicarboxyethylpyrrolenemethene-HCl, violet crystals, m. 190°, contg. 0.5 EtOH when recrystd. from EtOH and dried over  $P_2O_5$ . The perchlorate crystd. in the same manner when  $HClO_4$  was used in place of HCl. Di-Na salt, by treatment of the HCl or  $HClO_4$  salt with NaOH.  $p$ -Dimethylaminophenyl-2,4-dimethyl-3-carbethoxypyrrolenemethene- $HClO_4$  from  $p-Me_2NC_6H_4CHO$  and 2,4-dimethyl-3-carbethoxypyrrole with  $HClO_4$ . 2,5-Dimethyl-3-carbethoxy-4-dicarbethoxypyrrole, m. 81°, by refluxing 2,5-dimethyl-3-carbethoxypyrrole with  $MeOCH_2CO_2Et$ , and concd. HCl. 2,5-Dimethyl-3-carbethoxy-4-dicarboxyethylpyrrole, m. 195°, by sapon. of the preceding. 2,5-Dimethyl-3-carbethoxy-4-carboxyethylpyrrole m. 178°, by heating the preceding above its m. p. Hematinic acid, m. 96-7°, was prepd. by refluxing  $MeOCH_2CH(CO_2Et)_2$  with  $AcCH_2CO_2Et$  and  $ZnCl_2$ , addn. of HCN, and sapon. with loss of  $CO_2$ . A. W. DOX

Methylketole-yellow. B. ODDO. *Atti accad. Lincei* [vi], 1, 236-8(1923); cf. *C. A.* 17, 2881.—The action of phthalyl chloride on Mg 2-methylindyl bromide yields: (1) di-2-methylindylphthalide (methylketolephthalide),  $[C_8H_7NH.CMe:C_2C_6H_4.CO.O]$ , bright red micro-crystals, m. 258° (decompn.), and when heated with alc. KOH gives potassium 2-methylindyl 2-methylindolidenebenzylmethane- $o$ -carboxylate (methylketole-yellow),  $C_8H_7.NH.CMe:CC(C_6H_4.CO_2K):C.C_6H_4.N:CMe$ , the corresponding free acid

dyeing wool and silk red with violet reflection, even in 0.001% soln.; this coloration, which may be given also to cotton after mordanting, is stable to light, water, soap, or free alkali or acid. (2) A compd., which is resistant towards fused KOH and is possibly an isomeride of methylketolephthalide of the formula  $C_8H_7(COC:CMe.NH.C_6H_4)_2$ , its formation being due to the presence of sym. chloride in the phthalyl chloride used.

B. C. A.

Transformation of isatin to a tetrahydroquinazoline derivative. H. RUPE AND

G. A. GUGGENBUHL. *Helvetica Chim. Acta* 8, 358-60(1925).—Isatinphenylhydroxylamine and  $\text{SOCl}_2$  react with the evolution of  $\text{SO}_2$  and  $\text{HCl}$ ; the reaction product, poured on to ice, gives 3-phenyldiketotetrahydroquinazoline, m.  $272^\circ$  (Busch, *Ber.* 25, 2853 (1892)). C. J. Wesr

The chemistry of carbazole. HANS LINDEMANN AND WILHELM WESSEL. *Ber.* 58B, 1221-30(1925), cf. C. A. 19, 282.—Neither of the 2 methods hitherto known for the prepn of 1 aminocarbazole (I), viz. reduction of the 1- $\text{NO}_2$  compd. (II) or synthesis from 2,4 ( $\text{O}_2\text{N}$ ) $_2\text{C}_6\text{H}_3\text{Cl}$  (III), is satisfactory, as II can be obtained in only about 2% yield by nitration of carbazole, and III is formed in only very small amts in the compn of the 2,4-isomer from  $\text{O}_2\text{NC}_6\text{H}_4\text{Cl}$  and can be completely sep'd from this isomer only with difficulty. The present work was undertaken to find, if possible, some method of prepn in greater amt. one of the intermediate products in the synthesis of I. It was found in no way possible to prep smoothly 2,4-( $\text{O}_2\text{N}$ ) $_2\text{C}_6\text{H}_3\text{X}$  (X = halogen) by elimination of  $\text{CO}_2$  from the 4,3,5-X( $\text{O}_2\text{N}$ ) $_2\text{C}_6\text{H}_3\text{CO}_2\text{H}$  or of  $\text{SO}_2$  from the corresponding  $\text{SO}_2\text{H}$  acids, nor does 4,3,5-Cl( $\text{O}_2\text{N}$ ) $_2\text{C}_6\text{H}_3\text{CONH}_2$  undergo the normal Hofmann degradation; with Br and alkali in MeOH the Cl is replaced by MeO and heating the product with  $\text{HCl}$  in a sealed tube gives 4,3,5  $\text{HO}(\text{O}_2\text{N})_2\text{C}_6\text{H}_3\text{CO}_2\text{H}$  (IV). 3,5-Dinitro-4-chlorobenzoic acid (V) cannot be obtained through the hydrazide, for in the Et ester of this acid the Cl reacts more rapidly than the  $\text{CO}_2\text{Et}$  group with  $\text{N}_2\text{H}_4$ , but it can be obtained easily and in good yield from the acid chloride with  $\text{NaN}_3$  in AcOH. With concd.  $\text{H}_2\text{SO}_4$  V reacts explosively, but with more dil. acid on the water bath N is evolved vigorously with formation of 3,5-dinitro-4-chloroaniline (VI) (obtained in better yield from its Ac deriv., which can be smoothly prep'd by heating V with  $\text{Ac}_2\text{O}$  and a few drops concd.  $\text{H}_2\text{SO}_4$ ). On boiling with  $\text{H}_2\text{O}$  or dil. AcOH, V gives, together with VI, bis-[3,5-dinitro-4-chlorophenyl]urea (VII), which is obtained pure when V is heated in AcOH until the evolution of N ceases, and is also formed instead of the expected isocyanate in neutral solvents ( $\text{PhNO}_2$ ;  $\text{PhMe}$ ). Attempts to eliminate the  $\text{NH}_2$  group in VI by boiling the diazonium salt (solid or in soln) with alc. failed; even in the presence of Cu powder, only the phenol, together with resinous products, was obtained. When, however, the Ac deriv. of VI is heated with  $\text{PhNH}_2$  on the  $\text{H}_2\text{O}$  bath, the Cl is replaced by  $\text{PhNH}$  and the 4-amino-2,6-dinitrodiphenylamine (3,5-dinitro-4-aminoaniline) (VIII) obtained by hydrolysis of the product can be smoothly diazotized; the solid diazonium salt, heated with alc., gives 2,6-( $\text{O}_2\text{N}$ ) $_2\text{C}_6\text{H}_3\text{NHPH}$  (IX), used in the earlier work for the synthesis of I. It had been hoped to obtain VIII from 4,3,5 Cl( $\text{O}_2\text{N}$ ) $_2\text{C}_6\text{H}_3\text{CO}_2\text{H}$  by replacing the Cl by  $\text{PhNH}$  and converting the resulting acid (X) through the chloride into the azide (XI), but the latter, which is easily obtained, cannot be smoothly changed into the amine or its Ac deriv.;  $\text{H}_2\text{SO}_4$  or  $\text{Ac}_2\text{O}$  does not effect the reaction and AcOH gives bis-[3,5-dinitro-4-aminoaniline]urea (XIII). X, however, is readily reduced by  $(\text{NH}_4)_2\text{S}$  to 3-amino-4-amino-5-nitrobenzoic acid (XIV) which with  $\text{NaNO}_2$  smoothly yields 1-phenyl-7-nitrobenzotriazole-6-carboxylic acid (XV); this shows no tendency to lose N with formation of the carbazole ring, but the 7- $\text{NH}_2$  acid (XVI), heated with an excess of  $\text{BaO}$ , loses both  $\text{CO}_2$  and N and gives I in satisfactory yield. 4,3,5 Cl( $\text{O}_2\text{N}$ ) $_2\text{C}_6\text{H}_3\text{CO}_2\text{H}$  loses no  $\text{CO}_2$  on heating; it b.  $230^\circ$  without decompn. It and its salts decomp. explosively, with evolution of flames, when heated with alkalis or  $\text{BaO}$ . 3,5-Dinitro-4-chlorobenzenesulfonic acid, from  $\text{PhCl}$  with fuming  $\text{H}_2\text{SO}_4$  and  $\text{KNO}_3$ , m.  $293^\circ$ ; 4-Br analog m. above  $300^\circ$ . 3,5-Dinitro-4-chlorobenzoyl chloride, from the acid and  $\text{PCl}_5$  in  $\text{C}_2\text{H}_5$ , m.  $68^\circ$ . Amide (XVII), light yellow, m.  $186^\circ$ , from the chloride and cold concd.  $\text{NH}_4\text{OH}$ ; with hot  $\text{NH}_4\text{OH}$  is obtained 3,5-dinitro-4-aminobenzamide, yellow, m.  $252^\circ$ . 3,5-Dinitro-4-methoxybenzamide, from XVII with  $\text{NaOMe}$  or 3,5-dinitro-4-methoxybenzoyl chloride (XVIII, below) and  $\text{NH}_4\text{OH}$ , yellow, m.  $165^\circ$ , hydrolyzed by concd.  $\text{HCl}$  at  $120-40^\circ$  to IV. XVIII, from the acid and  $\text{PCl}_5$  in  $\text{C}_2\text{H}_5$ , m.  $42^\circ$ . Et 3,5-dinitro-4-hydroxybenzoate, from the 4-Cl ester and  $\text{N}_2\text{H}_4$ ,  $\text{H}_2\text{O}$  in cold alc., m.  $138^\circ$ . V, m.  $86^\circ$ . VII, yellow, m.  $295^\circ$  (decompn). VI, yellow, m.  $187-8^\circ$ ; Ac deriv., almost white, m.  $228^\circ$  (decompn), converted by  $\text{PhNH}_2$  on the  $\text{H}_2\text{O}$  bath into 3,5-dinitro-4-aminoacetanilide, red, m.  $216^\circ$ , which with  $\text{AcOH-H}_2\text{SO}_4$  is hydrolyzed to VIII, red, m.  $154^\circ$ ; this on diazotization in alc.  $\text{HNO}_3$  yields 3,5-dinitro-4-aminoazobenzene diazonium nitrate, yellow-brown, detonates violently on sudden heating or when struck, decomp.  $148^\circ$  with evolution of light on slow heating (the chloride, decomp.  $175^\circ$ , and the sulfate, decomp.  $180^\circ$  on slow heating, are not sensitive to shock but deflagrate on rapid heating); boiled with 66% alc., best in the presence of a little Cu powder, all 3 salts give IX, orange, m.  $107-8^\circ$ . 3,5-Dinitro-4-aminoaniline, from the acid (X) and  $\text{PCl}_5$  in  $\text{C}_2\text{H}_5$ , red, m.  $123^\circ$ ; azide (XI), pale red, m.  $135^\circ$ , deflagrates on rapid heating. XIII, dark red, m.  $252^\circ$  (decompn). XIV m.  $239^\circ$ . 2-Methyl-1-phenyl-7-nitrobenzimidazole-5-carboxylic acid, from XIV and  $\text{NaOAc}$  in boiling  $\text{Ac}_2\text{O}$ , faintly yel-

low, m. 289°. XV, m. 279°, reduced by  $\text{SnCl}_2$  and  $\text{AcOH}\cdot\text{HCl}$  to XVI, m. 218° (*HCl salt* m. 237°; *Ac deriv* m. 281-2°) C. A. R.

Salt formation of imidazole-4,5-dicarboxylic acid. KURT LEHMSTEDT, *Ber.* 58B, 1219-20 (1925).—As the older investigators had characterized imidazole-4,5-dicarboxylic acid (I) as a monobasic acid, it did not surprise L. that by evapn. of its  $\text{NH}_4\text{OH}$  soln. he should have obtained an acid salt,  $\text{C}_3\text{H}_2\text{O}_4\text{N}_2\cdot\text{NH}_3$ . Pauly and Ludwig, however, have since (*C. A.* 16, 4210) described it as a dibasic acid and detd. the conductivities of the 1st and 2nd stages of dissociation by electrolyzing the Na salt obtained by neutralizing I to phenolphthalein with  $\text{NaOH}$ . L. now finds that on titrating I with 0.1 *N*  $\text{NaOH}$  only 87% of the I or 74% of the 2nd  $\text{CO}_2\text{H}$  group is satd., the end point is not sharp. As basicity detns with too weak acids which form no neutral salt cannot be made, P and L's values cannot be correct. Conc'n of a Na salt soln neutral to phenolphthalein gives first the difficultly sol. Na H salt and from the mother liquors alc. ppts. the Na<sub>2</sub> salt which in  $\text{H}_2\text{O}$  naturally dissolves with alk. reaction. The di- $\text{NH}_4$  salt, obtained from I in conc'd  $\text{NH}_4\text{OH}$  by pptn. with alc., decomps. at room temp. and loses completely the  $\text{NH}_3$  attached to the 2nd  $\text{CO}_2\text{H}$  group. Heating the acid Ca or Ba salts of I gives no ketone but only imidazole and decompn. products, such as  $\text{HCN}$ . C. A. R.

Configuration of nicotine. Optically active hygrinic acid. P. KARRER AND ROSE WIDMER, *Helvetica Chim. Acta* 8, 364-8 (1925).—Nicotine *py*-methiodide-HI (100 g.) is oxidized by alk.  $\text{K}_2\text{Fe}(\text{CN})_6$  giving 8 g. *N*-methylnicotine, b.p. 143-5°, m. 80°,  $[\alpha]_D^{20}$  -55.87° (0.1958 g. in 13.343 g. soln. in  $\text{H}_2\text{O}$ ), it titrates as a mono acid base. Further oxidation with  $\text{CrO}_3\cdot\text{H}_2\text{SO}_4$  gives 25% of *l*-hygrinic acid, m. 116°,  $[\alpha]_D^{20}$  -80.12° (0.1075 g. in 6.7294 g. of soln. in  $\text{H}_2\text{O}$ ); Cu salt, deep blue needles. MeI and  $\text{Ag}_2\text{O}$  in MeOH transform this into *l*-stachydrine, identical with the natural product. Since *l*-stachydrine has been prep'd. from natural *l*-proline, this work proves that the 3 natural pyrrolidine compds., *l*-proline, *l*-stachydrine and *l*-nicotine, have the same configuration. C. J. WEST

*l*-Truxinic acid. IX. R. STOERMER AND P. KLOCKMANN, *Ber.* 58B, 1164-78 (1925); cf. *C. A.* 18, 2172.—The configuration of *l*-truxinic acid (I) was established (*C. A.* 13, 1889) by its resolution into 2 optically active antipodes, a property of only a single *cis*-di- $\text{CO}_2\text{H}$  acid among the 6 theoretically possible truxinic acids. Moreover, this is the only *cis*-acid among the 6 which can form 2 different monoesters, monoamides or monoanilides. One of each pair of these compds. had already been prep'd. and R. and K. have now been able to prep. their isomers, thus confirming the correctness of the configuration assigned to I. The  $\alpha$  mono-Me ester (II), m. 198°, previously obtained as a by-product in the esterification of I with  $\text{MeOH}\cdot\text{HCl}$ , is also easily obtained from the anhydride (III) of I and boiling MeOH but by no other esterification method nor by partial sapon. of the di-Me ester, as rearrangements cannot be avoided. The  $\alpha$ -mono anilide (IV), from III and  $\text{PhNH}_2$ , m. 214° (instead of 209°) when pure; the product obtained from the phenylimide (V) of I with alc. KOH is a mixt., m. about 209°, of *l*-truxinanilidic acid (VI), m. 225°, and of *b*-IV, m. 237°, the 2 acids can be sep'd. quite readily, as the *b*-IV is very difficultly sol. in various solvents and forms a very difficultly sol. Na salt. On long treatment with alc. KOH, *b*-IV quant. rearranges into VI. *a*-IV differs from the *b*-acid in forming a very easily sol. Na salt, in not being converted into VI by cold alc. KOH and in its solubilities; long boiling with AcOH converts both into V. Esterification of *b*-IV with  $\text{MeOH}\cdot\text{HCl}$ ,  $\text{CH}_3\text{N}_2$ , or alk.  $\text{Me}_2\text{SO}_4$  gives, without change in configuration, *a*-Me *l*-truxin-*a*-anilide (VII), m. 244°; and *a*-IV with  $\text{CH}_3\text{N}_2$  or  $\text{Me}_2\text{SO}_4$  yields *b*-Me *l*-truxin-*a*-anilide (VIII), m. 234°, but with  $\text{MeOH}\cdot\text{HCl}$  is obtained a mixt. from which only VII and never VIII can be isolated; this can be explained only by assuming that V is formed as an intermediate product; in fact, V with  $\text{MeOH}\cdot\text{HCl}$  gives VII. Similarly, both VII and VIII with alc. KOH yield mixts. contg., besides VI, only *b*-IV; here, too, V must be an intermediate product, although it could not be isolated. The behavior of the IV and their esters can be explained only by assuming that the  $\text{CONHPh}$  group occupies different positions in the 2 acids, as shown in formulas XVII and XVIII. The yellow *N*-NO deriv. (IX) of *b* IV is very stable and on dry heating splits off  $\text{HNO}_2$ , chiefly with formation of V; with cold KOH it gives almost pure I. *a*-IX, on the other hand, is very unstable and decomps. and deliquesces in 20-25 min.; with alkalis or hot  $\text{H}_2\text{O}$  it gives pure I. The *N*-NO deriv. (X) of VIII, however, is stable and is not decompd. by boiling  $\text{H}_2\text{O}$ . Conc'd KOH is not suitable for hydrolyzing the  $\text{CONHPh}$  group alone of the esters of the IV, because it also partially attacks the  $\text{CO}_2\text{Me}$  groups, but with hot  $\text{Na}_2\text{CO}_3$  VII gives *a*-II while VIII yields *b*-II, m. 201°; the mixed II m. about 170°. *b*-II with  $\text{SOCl}_2$  and then  $\text{PhNH}_2$  smoothly regenerates the  $\text{Na}_2\text{CO}_3$ -insol. VIII, showing that no hydrolysis of the  $\text{CO}_2\text{Me}$  group has occurred

in these processes, similarly, *a*-II regenerates VII. With  $\text{SOCl}_2$  and  $\text{NH}_3$ , *a*- and *b*-II give resp. *a* *Me*  $\zeta$ -truxin *b* amide (XI), m  $195^\circ$ , and *b*-*Me*  $\zeta$ -truxin-*a*-amide (XII), m  $212^\circ$ . XI can also be obtained from the previously known *b*-amidic acid (XIII), m  $222^\circ$  (prepd by cautious sapon with alc. KOH of the imide (XIV) of I, with  $\text{CH}_3\text{N}$ , or through the Ag salt with MeI, but not with  $\text{MeOH}\cdot\text{HCl}$  or alk.  $\text{Me}_2\text{SO}_4$ , *a*-XIII, m  $204^\circ$  has now been obtained from III and dry  $\text{NH}_3$  in  $\text{C}_6\text{H}_6$ ; boiling 50% AcOH rapidly hydrolyzes it to I, while the *b*-XIII undergoes this hydrolysis much more slowly and probably not quant. Both XIII smoothly yield I in AcOH with  $\text{HNO}_3$ . Unlike *b*-XIII, the *a*-acid is esterified by  $\text{Me}_2\text{SO}_4\cdot\text{Na}_2\text{CO}_3$  to XII. XI and XII in AcOH with  $\text{HNO}_3$  smoothly yield *a*- and *b*-II, resp. All the above substances



melt with foaming (which is characteristic of *cis*-di  $\text{CO}_2\text{H}$  deriva. of the truxio series); all the *a*-derivs melt lower than the *b*-forms; the *a*-IV and -XIII are exceedingly easily sol. in many solvents and their Na and  $\text{NH}_4$  salts quite easily sol. in  $\text{Na}_2\text{CO}_3$  and  $\text{NH}_4\text{OH}$ , resp., while the *b*-acids and their salts are difficultly sol. or insol. The 2 XIII are quite stable towards cold 10% alc. KOH but on 5 min. boiling the *b*-acid rearranges into  $\delta$ -truxin-*amidic* acid, m  $189^\circ$  (also obtained from  $\delta$ -truxindiamide or XIV and boiling 10% alc. KOH), while the *a*-acid is unchanged. Of the esters of the IV and XIII, only that of *b*-XIII has a normal lower m p than the corresponding acid. *a* XIII with  $\text{MeOH}\cdot\text{HCl}$  yields a mixt of XII and (free) *b*-XIII, which is assumed to be formed through XIV as an intermediate product. When the chloride of I is treated with  $\text{AlCl}_3$  as in the prepn. of truxone from  $\alpha$  truxillic acid (C. A. 14, 55) no truxinone is formed, but the reaction mixt. treated with  $\text{Na}_2\text{CO}_3$  contains a satd acid, m  $155^\circ$ , contg 1 mol  $\text{H}_2\text{O}$  less than I, which titrates as a monobasic acid and forms an oxime, m  $220^\circ$ ; it is assigned the structure XV and is designated as  $\zeta$ -hemitruxinonic acid; unfortunately, it cannot be converted back into I or  $\delta$  truxinic acid by fusion with alkali as it undergoes deep-seated decompn with formation of unsatd. acids. If, now, the chloride, m  $120^\circ$ , of *b*-II is similarly treated with  $\text{AlCl}_3$ , it yields the *Me* ester (XVI), m  $88^\circ$ , of XV (also obtained from XV and  $\text{MeOH}\cdot\text{HCl}$ ), while the chloride, m  $104\text{--}5^\circ$ , of *a*-II gives no homogeneous product and at any rate no XVI. This shows that in the above monoesters, -amides and -anilides of I, the *a*- and *b*-forms have the structures XVII and XVIII, resp. The I, m  $239^\circ$ , is obtained purer and in better yield than by the method previously given by following the scheme:  $\delta$  truxinic acid  $\rightarrow \text{NH}_4$  salt  $\rightarrow \text{XIV} \rightarrow \text{XIII} \rightarrow \text{I}$ . VI is obtained in 5 g yield from 10 g  $\delta$ -truxinic acid heated 25 min at  $160\text{--}70^\circ$  with excess of  $\text{PhNH}_2$ ; it is unchanged by standing several days in 40% alc. KOH, but 6 g heated 4 hrs. at  $150^\circ$  with  $\text{NaOAc}$  and  $\text{Ac}_2\text{O}$  gives 3 g. V, m  $150\text{--}1^\circ$ . C. A. R.

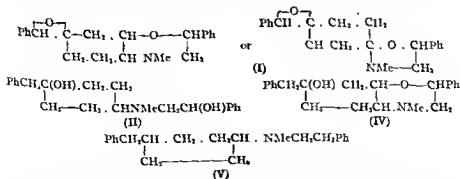
The hydroferrocyanides and hydroferricyanides of the alkaloids. W. M. CUMMING AND D. C. BROWN, *J. Soc Chem Ind* 44, 110-5T (1925)—Hydroferrocyanic acid was prepd by mixing 40 cc satd.  $\text{K}_3\text{Fe}(\text{CN})_6$  with 40 cc. concd.  $\text{HCl}$ , filtering off the  $\text{KCl}$ , and shaking the filtrate with 70 cc.  $\text{Et}_2\text{O}$ . The middle oily layer was dried in vacuum, and the residue dissolved in alc. With hydroferrocyanic acid, in acid soln., cinchonine yielded brownish needles,  $\text{BA}\cdot 2\text{H}_2\text{O}$  (B = alkaloid, A = acid); quinine, a yellow ppt of  $\text{BA}\cdot 2\text{H}_2\text{O}$ , which on standing became anhyd.; phenazone, white crossed prisms,  $\text{B}_2\text{A}$ ; pyramidone, bluish green prisms,  $\text{BA}\cdot 2\text{H}_2\text{O}$ ; cocaine, white plates,  $\text{B}_2\text{A}\cdot 2\text{H}_2\text{O}$ , decompd on heating; narcotine,  $\text{B}_2\text{A}\cdot 2\text{H}_2\text{O}$ ; brucine,  $\text{BA}\cdot 2\text{H}_2\text{O}$ ; strychnine,  $\text{BA}\cdot 2\text{H}_2\text{O}$ . With a neutral soln. of hydroferrocyanic acid, cinchonine gives a red coloration, changed by the addn. of  $\text{HCl}$  first to a buff powder and then to lemon-yellow crystals,  $\text{BA}\cdot \text{H}_2\text{O}$ , quinine an orange-yellow ppt,  $\text{B}_2\text{A}\cdot 2\text{H}_2\text{O}$ ; phenazone,  $\text{B}_2\text{A}$ ; pyramidone, no ppt.; cocaine,  $\text{B}_2\text{A}\cdot 3\text{H}_2\text{O}$ ; narcotine,  $\text{B}_2\text{A}\cdot 2\text{H}_2\text{O}$ ; brucine,  $\text{BA}$ ; strychnine,  $\text{BA}$ . In alc. soln., cinchonine yields with hydroferrocyanic acid  $\text{BA}\cdot 1.5\text{EtOH}$ ; quinine, an orange ppt. which loses alc and becomes green,  $\text{B}_2\text{A}$ ; phenazone,  $\text{BA}\cdot 2\text{EtOH}$ ; pyramidone, with an excess of base,  $\text{BA}\cdot 2\text{EtOH}$ ; with an excess of acid,  $\text{B}_2\text{A}\cdot \text{EtOH}$ ; cocaine,  $\text{B}_2\text{A}\cdot \text{EtOH}$ ; narcotine,  $\text{B}_2\text{A}$ ; brucine,  $\text{BA}\cdot 2\text{EtOH}$ ; strychnine,  $\text{BA}\cdot 2\text{EtOH}$ . With hydroferrocyanic acid in acid soln., cinchonine yields yellow plates,  $\text{BA}\cdot 2\text{H}_2\text{O}$ ; quinine, orange-yellow crystals,  $\text{BA}\cdot 3\text{H}_2\text{O}$ ; phenazone, yellow plates,  $\text{B}_2\text{A}\cdot 4\text{H}_2\text{O}$ ; pyramidone, unstable yellow plates; cocaine, yellow plates,  $\text{B}_2\text{A}$ ; narcotine, unstable; brucine, yellow ppt,  $\text{B}_2\text{A}\cdot 6\text{H}_2\text{O}$ ; strychnine, silky yellow needles,  $\text{B}_2\text{A}\cdot 6\text{H}_2\text{O}$ . With hydroferricyanide acid in alc. soln. cinchonine yields  $\text{BA}\cdot \text{EtOH}$ , quinine, yellow ppt.,  $\text{BA}\cdot 2\text{EtOH}$ ; phenazone, yellow needles,  $\text{B}_2\text{A}\cdot \text{EtOH}$ , pyramidone, greenish plates,  $\text{B}_2\text{A}\cdot \text{EtOH}$ ; cocaine, yellow plates,  $\text{B}_2\text{A}\cdot \text{EtOH}$ ; brucine, amorphous ppt.,  $\text{B}_2\text{A}$ ; strychnine, yellow needles,  $\text{B}_2\text{A}$ .

T. S. CARSWELL

**Constitution of the morphine alkaloids. III. HEINRICH WIELAND AND MUNIO KOTAKE.** *Ann* 444, 69-93(1925), cf *C A* 18, 273.—The introduction discusses the present state of the constitution of morphine and thebaine *des-N-Methylidihydrocodeinone oxime*, m. 191-25°. *Dihydro-des-N-methylidihydrothebaine* (I) does not cryst.; the methiodide (II) m. 217-22°, with excess 2 N HCl I gives 80% of *dihydro-des-N-methylidihydrocodeinone* (III), softens 95°, m. 110°, methiodide, m. 295°; *oxime*, m. 153-5° (HCl salt, m. 271-2°). *Dihydro-des-N-methylidihydrocodeine perchlorate*, m. 218-9°; *chloroplatinate*, m. 202°; *nitrate*, m. 174-5°, concd. HNO<sub>3</sub> gives the *nitro nitrate*, yellow, m. 220-1°. Oxidation of the ketones gives III. II, shaken with Ag<sub>2</sub>O, and the residue heated at 205°, splits off Me<sub>2</sub>N and gives a compd., C<sub>15</sub>H<sub>15</sub>O<sub>2</sub>, m. 119°, strongly unsatd. towards KMnO<sub>4</sub>, and on catalytic hydrogenation gives the compd. C<sub>15</sub>H<sub>21</sub>O<sub>2</sub>, m. 148-50°, MeOH being split off. The latter is a phenol, sol in dil EtOH-KOH and gives a characteristic green FeCl<sub>3</sub> reaction. *Dihydro-des-N-methylidihydrothebainone*, m. 154-6°, gives a green color reaction with FeCl<sub>3</sub>, this is most conveniently prepd. by catalytic reduction of *des-N-methylidihydrothebaine Picrate*, yellow, m. 185-8°. *Ac picrate*, m. 188-92°. *Methiodide* (IV) m. 226-9°. *Piperonylidene compd.*, light yellow, m. 179-81°; concd. H<sub>2</sub>SO<sub>4</sub> and HCl give orange colored halochromism, excess piperonal and EtONa for 2 days give the compd. C<sub>22</sub>H<sub>21</sub>O<sub>4</sub>N, yellow, m. 179-81°, probably an addn. compd. of EtOH to the double bond. *Piperonylidenedihydrothebainone*, yellow, m. 174-5°; concd. HCl gives an orange-red halochromism, FeCl<sub>3</sub> a green color. IV, distd. with an excess of 10% NaOH, splits off Me<sub>2</sub>N and gives 80% of thebenone, C<sub>15</sub>H<sub>13</sub>O<sub>2</sub>, m. 134-6°; *oxime* m. 201-4°. *Isonitroso deriv.*, pale yellow, m. 165° (decompn.). *Benzal deriv.* m. 162°; *piperonal deriv.* m. 155-6°. Oxidation gives a *diketone*, C<sub>17</sub>H<sub>15</sub>O<sub>4</sub>, m. 185-7°; *dioxime* m. 260°; an *isomeric dioxime*, m. 236-9°, results from the isonitroso deriv.

C. J. WEST

**Lobelia alkaloids. II. HEINRICH WIELAND, CLEMENS SCHOPF AND WILHELM HERMSEN.** *Ann* 444, 40-68(1925), cf *C A* 16, 1071.—The mother liquor from the prepn. of lobeline upon removal of the solvent yields a thick yellow sirup; neutralized with 2 N EtOH-HCl or -HBr at 0°, there ppts. after addn. of Et<sub>2</sub>O the salt of *lobelanine* (I); the free base is liberated by treating the hot satd. soln. with excess ice-cold Na<sub>2</sub>CO<sub>3</sub>. I, m. 99°, is optically inactive, gives no color with concd. H<sub>2</sub>SO<sub>4</sub> or HNO<sub>3</sub> and slowly gives a brownish yellow color with Frohde reagent; it is not reduced by Pd and H<sub>2</sub>, does not contain an active H atom (MeMgI) but apparently reacts with this reagent. BzCl is without action as is NaNO<sub>2</sub> or CH<sub>3</sub>N<sub>3</sub>. HI does not split off an alkyl group. *HCl salt* m. 188°; *HBr salt* m. 188°; *HI salt* m. 169-72°; *perchlorate* m. 173-4°; *nitrate* m. 153-4°. Oxidation of I with CrO<sub>3</sub> gives BzOH and MeNH<sub>2</sub>; with KMnO<sub>4</sub>, 2 mols. BzOH. I is very stable towards HNO<sub>3</sub> (d 1.4). Heated to 140°, there results 17% of BzMe; this is increased to 48% by heating in BzOH 3-4 min. at 140°. Dil. HCl of BzMe; in a sealed tube at 120-30° gives BzMe, fluorene and MeNH<sub>2</sub>. Alkali gives PhMe-CHOH, Ph<sub>2</sub>CHOH and MeNH<sub>2</sub>, the PhMeCHOH results by the action of the alkali on the BzMe; the Ph<sub>2</sub>CHOH from the Ph<sub>2</sub>CO. Ph<sub>2</sub>CO in addn. to the yellow *p-nitro-*



phenylhydrazones, m. 154°, was isolated as a wine-red form, m. 144°; repeated crystn. gave the higher melting form. The mother liquor from I, dild. with H<sub>2</sub>O, freed from EtOH and Et<sub>2</sub>O by distg. in *vacuo*, treated with 0.1 mol. N NaOH which ppts. a brown smear and the clear soln. treated with KNO<sub>3</sub> ppts. a *nitrate*, m. 212-3°, of *lobelanidine* (II), m. 150°, optically inactive, dists. undecompd. in a high vacuum, is not oxidized by CrO<sub>3</sub> in AcOH, is very slowly oxidized by HNO<sub>3</sub>. *HCl salt* m. 135-8°; *HBr salt*

m 188-90° I is reduced to II by Na-Hg in dil. AcOH. *Di-Ac deriv.*, m. 214-5°, whose acetate m 75°. *Di-Bz deriv.* (III) m 109-10°; *HCl salt* m. 239-40° (decompn.). II *Mel* m 173-5° but does not clear until 200°. Ag<sub>2</sub>O in dil. Me<sub>2</sub>CO gives the hydroxide m 152°; thermal decompn gave only about 25% of the N as volatile bases; a part of it resublimed and a part was recovered as II. III. *Mel* m 156° (decompn.); the free base, heated to 170-80° *in vacuo* gave some BzMe and BzOH but the residue was principally III. Distd with anhyd. Al<sub>2</sub>O<sub>3</sub>, II gave a small amt. of BzMe. II and PCl<sub>5</sub> give *dichlorolobelan*, analyzed as the *HCl salt*, m 158-9° (decompn.). This is reduced by Al to *lobelan* (V), b about 175° in a high vacuum; *HCl salt* m. 194-5°; *methiodide* m 234-5°, the base, liberated by Ag<sub>2</sub>O in dil. Me<sub>2</sub>CO, on distn at 180°, gave only traces of volatile bases. The previous formula for lobeline (IV), C<sub>20</sub>H<sub>27</sub>O<sub>2</sub>N, must be changed in the light of the above work to C<sub>20</sub>H<sub>25</sub>O<sub>2</sub>N. IV is reduced to II by Na-Hg. *Bz deriv.* of IV, isolated as the *HCl salt*, with 1 H<sub>2</sub>O, m 155-7° (decompn.). IV and PCl<sub>5</sub> give *chlorolobelan-HCl*, m 172-4° (decompn.). The mother liquors from the purification of II yield *isolobelanine*, C<sub>20</sub>H<sub>25</sub>O<sub>2</sub>N, m 120-1°, optically inactive, *nirrate* m 193° (decompn.), *HCl salt* m 201-2°; *methiodide* m. 183-4°. It contains no HO group since it does not react with BzCl in C<sub>6</sub>H<sub>5</sub>N. Heating splits off BzMe. Reduction with Na-Hg does not give II, but *isolobelanidine* (?), whose *HCl salt* m. 247-8°. *α-Phenethylcyclohexylamine*, b<sub>p</sub> 135°, from C<sub>6</sub>H<sub>11</sub>NH<sub>2</sub> and PhCH<sub>2</sub>CH<sub>2</sub>Br. *HBr salt* m 251-2°. Exhaustive methylation gives *α-phenethylmethylcyclohexylamine-Mel*, m 149°, the action of Ag<sub>2</sub>O followed by distn at 120° gives styrene and *cyclohexyldimethylamine*, whose *HBr salt* m 197°. *β-Phenethylcyclohexylamine*, b<sub>p</sub> 152°, b<sub>p</sub> 164°; *HBr salt* m 232-3°. A *tert base*, (PhCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NC<sub>6</sub>H<sub>11</sub>, whose *HBr salt* m. 168°, also appears to be formed. *β-Phenethylmethylcyclohexylamine-Mel* m 133°. The Hofmann degradation gives styrene and cyclohexyldimethylammonium bromide, m. 197°. *Di-β-phenethylmethylamine* b<sub>p</sub> 188°; *picrate* m 101°. C. J. West

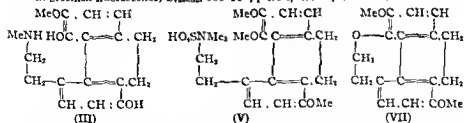
**Preparation of bromo- and chlorocodeine and their behavior on catalytic reduction.** EDMUND SPEYER AND HANS ROSENFELD. *Ber.* 58B, 1110-3(1925)—If the proper conditions are not carefully adhered to in Anderson's method of prepg. chlorocodeine (I) (*Ann.* 77, 369(1851)), amorphous products sometimes result. S and R. have accordingly simplified and improved the method; codeine-HCl (II) in 30% HCO<sub>2</sub>H and 30% H<sub>2</sub>O<sub>2</sub> react with vigorous foaming when warmed and NaOH ppts I in good yield. Bromocodeine (III) is obtained in the same way from codeine-HBr (IV). III shaken with Pd-charcoal and H in 10% AcOH absorbs 1 mol H<sub>2</sub> in a few min, giving *monobromodihydrocodeine* (V) which on further reduction absorbs a 2nd mol of H<sub>2</sub> in the course of several hrs, yielding *dihydrocodeine*. From I, it is possible to obtain only *monochlorodihydrocodeine* (VI). I (3 g. from 5 g. II), m 175-6°, [α]<sub>D</sub><sup>20</sup> -47.21° (alc., c 1.0048). III (3.5 g. from 5 g. IV), m 162°. V (2 g. from 3 g. IV), m 180°. VI (yield, quant.), m. 196°. C. A. R.

**Action of thionyl chloride on codeine and its isomers.** EDMUND SPEYER AND HANS ROSENFELD. *Ber.* 58B, 1113-6(1925)—Knorr and Hörlem (C. A. 2, 644) found that the *α-chlorocodide* (I) obtained from codeine and PCl<sub>5</sub> is isomerized by hot fuming HCl under pressure into *β-chlorocodide* (II). The same rearrangement can be effected by heating I above its m. p. (Pechor and Rollett, C. A. 4, 2132); the yields of II are better than by the K. and H. method, but as superheating results in a sudden decompn. of the entire material S and R. did the heating in indifferent solvents boiling in the vicinity of the m. p. of I (tetralin and PhBr). Even in boiling tetralin I undergoes some slight decompn. in 1 hr. but in PhBr there is no decompn. and in both cases II can be smoothly isolated from the reaction mixt. Hydrolysis of I or II in dil. AcOH yields 3 isomers of codeine (isocodeine (III), pseudocodeine (IV) and allospseudocodeine (V)) (K. and H.). From IV K. and H. with PCl<sub>5</sub> obtained I and an oily product yielding a cryst. methiodide (C. A. 4, 447). S and R. with SOCl<sub>2</sub> have now obtained I but never an oily pseudochlorocodide, and from V they quant. obtained II, with which the allospseudochlorocodide of S and Kraus (C. A. 17, 3508) is therefore identical; III likewise yields II quant. The formation of II from codeine and IV with fuming HCl under pressure (K. and H.) is the result of a secondary isomerization of I formed primarily. Why chlorination of codeine and IV (with SOCl<sub>2</sub>) should yield I and that of III and V should give exclusively II cannot satisfactorily be explained at the present stage of morphine chemistry. Attempts to hydrolyze Freund's dihydrochlorocodide (C. A. 15, 834) by K.'s method were unsuccessful. II, m. 153°, is obtained in 50% yield from I refluxed 1 hr. in tetralin and in 70-5% yield in PhBr. I (11 g. from 12 g. IV in SOCl<sub>2</sub> in ice), m 148°, [α]<sub>D</sub><sup>20</sup> -385.2° (alc., c 0.9264). C. A. R.

**Action of sodium hyposulfite on bromocodeinone.** EDMUND SPEYER AND HANS

ROSENFELD *Ber.* 58B, 1117-9(1925)—Freund's bromocodeinone (I) (*Ber.* 39, 844 (1906)) apparently yields different reduction products, depending on the nature of the reducing agent used, with Fe and  $H_2SO_4$  F obtained the same codeinone as was prepd. by Ach and Knorr (*Ber.* 36, 3067(1903)) from codeine with  $CrO_3$ , while S. and Sarre (*C. A.* 19, 297) with Pd and H obtained dihydrocodeinone and by electrolytic reduction at prepd. Pb electrodes a new dihydrodesoxycodeine. S and R now find that with  $Na_2S_2O_4$  soln it yields a deep red liquid changing on heating to light brown, with deposition of S. Addn of NaOH to the ice-cold soln ppts a white, amorphous, halogen-free base (II) which does not cryst itself nor yield cryst salts. On heating with NaOH it dissolves with brown color and at the same time there seps a cryst base,  $C_{18}H_{21}O_2N$  (III), contg. a tertiary N atom, as shown by the formation of an amorphous methiodide, and a C:O group, detected as the oxime. III is insol in fixed alkalies and therefore contains the O bridge intact, only on electrolytic reduction at prepd. Pb electrodes does it yield an alkali-sol. amorphous product forming amorphous derivs and therefore not studied further. Attempts to reduce III with Pd and H failed, indicating that the aliphatic double bond has been satd. It is suggested that under the influence of the  $Na_2S_2O_4$  the Br in I is replaced by H and the product rearranges into the enol form of dihydropseudocodeinone, which is converted by hot NaOH into the keto form (II). Attempts to reduce I with Na or Na-Hg in alc failed. II (15 g. from 12 g. I), decomp.,  $240-1^\circ$ ; picrate, yellow, gradually decomp. about  $210^\circ$ , oxime, decomp.  $266-70^\circ$ , sol. in fixed alkalies, reppd unchanged from NaOH by  $NH_4Cl$ . C. A. R.

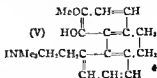
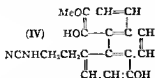
Dihydrothebenine and its degradation. EDMUND SPEYER AND HANS ROSENFELD, *Ber.* 58B, 1120-4(1925)—Thebenine (I) cannot be reduced electrically, with Pd-H or Na and alc. but in  $H_2O$  with  $Na_2S_2O_4$  it yields a cryst thiosulfate,  $(C_{18}H_{21}O_2N)_2 H_2S_2O_4$  (II) of dihydrothebenine (III), which, like I, can neither be acetylated nor benzoylated; heated with MeI under pressure, it gives *N*-methyl-dihydrothebenine-HI (IV), which cannot be exhaustively methylated owing to the instability imparted to it by its phenolic character. III, however, shaken with alk.  $Me_2SO_4$  gives dimethoxydihydrothebenine-methine-Me sulfate (V) converted in  $H_2O$  by KI into the methiodide,  $C_{18}H_{21}O_2NMe_2I$  (VI); this, converted with moist  $Ag_2O$  into the hydroxide and boiled with alkali, loses  $NMe_2$  and the Me on the 4-HO group, which now forms a new ring with the adjacent vinyl group, the product being methoxydihydrothebenol (VII). Heated with HI and red P under pressure, VII yields an oil (VIII) forming a cryst. picrate but not enough was obtained to det. whether it is a dihydropyrene analogous to the pyrene not obtained by Freund from thebenol. II (5 g. from 6 g. I.HCl), m.  $194-5^\circ$ . III (1 g. from 2 g. II in  $Me_2CO$  suspension slowly treated with dil.  $NH_4OH$  until dissolved and then with  $H_2O$  to a faint permanent turbidity), rodlets with 1  $H_2O$ , decomp.  $147-8^\circ$ , also slowly at  $100^\circ$ , easily sol. in fixed alkalies, reppd unchanged from NaOH by  $NH_4Cl$ ;  $HCl$  sol., yellowish, decomp.  $237-8^\circ$ , optically inactive (1% soln. in a 22-dm. tube). IV (0.8 g. from 1 g. III), m.  $130-1^\circ$ . V (yield, quant.), decomp.  $270-1^\circ$ . VI (1.5 g. from 2 g. V), decomp.  $245^\circ$ . VII (1.8 g. from 5 g. VI), m.  $133-4^\circ$ , insol. in alkalies. VIII, oil with greenish fluorescence,  $b_{\text{vacuum}}$   $300-10^\circ$ ; picrate, decomp.  $212-4^\circ$ .



C. A. R.

Action of bromocyanogen on thebaine. EDMUND SPEYER AND HANS ROSENFELD, *Ber.* 58, 1125-8(1925).—v. Braun (*C. A.* 8, 3303) found that when thebaine (I) in  $CHCl_3$  is treated with  $BrCN$  and then with  $Et_2O$ ,  $LHBr$  is pptd. and the filtrate on evapn. yields an oil which, from its Br content, he assumed to be a  $BrCN$  addn. product of I and which, on long chilling and digestion with cold  $Et_2O$ , yields (in minimal amt.) a compd. (II) to which he assigned the formula  $C_{20}H_{23}O_2N_2$ . On repeating v. B.'s work, S. and R. confirmed his observation as to the smallness of the yield of II, but found that it can be obtained much more quickly and in much greater yield (about 50%) by treating I in  $AcOH$ , gently warmed, with  $BrCN$  and then adding  $H_2O$ . It, however, has the compn.  $C_{18}H_{21}O_2N_2$  instead of that assigned to it by v. B. The solns. of I both

in  $\text{CHCl}_3$  and in  $\text{AcOH}$  become brown-red on treatment with  $\text{BrCN}$ , which suggested that the I might rearrange into thebenine (III) and that II is a deriv. of III, and as a matter of fact Zeisel detns. showed that II contains only 1, not 2,  $\text{MeO}$  groups. Moreover, II is sol. in fixed alkalis. It is therefore believed to be *norcyanothebenine* (IV), although attempts to prep. it from III and  $\text{BrCN}$  or to hydrolyze it to northebenine failed. On catalytic hydrogenation it absorbs 4 mols.  $\text{H}_2$  and yields an oily base forming with  $\text{MeI}$  a cryst. compd.  $\text{C}_{10}\text{H}_{17}\text{O}_2\text{NI}$  to which is assigned the structure V. IV, m.  $146-7^\circ$ , sol. in hot fixed alkalis and reprecip. unchanged by  $\text{NH}_4\text{Cl}$  if the heating has not been too vigorous and long continued. V (1 g. from 6 g. IV), m.  $298-9^\circ$ .



C. A. R

Compounds of amino acids with piperazines. EMIL ABDERHALDEN AND ERNST ROSSNER *Z. physiol. Chem.* 144, 219-33 (1925).—Synthesis of several piperazine peptides was performed by condensation of  $\alpha$ -halogen acid halides with piperazine and treatment of the reaction product with  $\text{NH}_3$ . *Di*[chloroacetyl]piperazine (I), m.  $137^\circ$ , was prepd. in 75-80% yield from piperazine,  $\text{ClCH}_2\text{COCl}$  and  $\text{NaHCO}_3$ . *Diglycyl*piperazine (II), amorphous and insol. in all solvents, by treatment of I with alc.  $\text{NH}_3$ . After hydrolysis piperazine can be recovered but no glycine. *Dihippuryl*piperazine, m.  $200^\circ$ , by benzoylation of II and crystn. from  $\text{EtOH}$ . *Picric acid deriv.* of II m.  $221^\circ$ . *Di*[ $\alpha$ -bromopropionyl]piperazine (III), m.  $162^\circ$  (yield 50%), by condensation of piperazine with  $\text{MeCHBrCOBr}$  and  $\text{NaHCO}_3$ . *Dialanyl*piperazine *di-HBr*, from III and alc.  $\text{NH}_3$ , free base, by treatment with  $\text{Ag}_2\text{SO}_4$  and  $\text{Ba(OH)}_2$ ; *di-Bz deriv.*, m.  $237^\circ$ . *Di*[ $\alpha$ -bromoisocaprolyl]piperazine (IV), m.  $141-2^\circ$ , in 67-70% yield from piperazine,  $\text{Me}_2\text{CHCH}_2\text{CHBrCOCl}$  and  $\text{NaHCO}_3$ . *Dileucyl*piperazine *di-HBr*, from IV and alc.  $\text{NH}_3$ ; free base (V) m.  $118-21^\circ$ ; *Bz deriv.*, m.  $244^\circ$ . *Di*[chloroacetyl]leucyl]piperazine (VI), m.  $223^\circ$  (decompn.), from V,  $\text{ClCH}_2\text{COCl}$  and  $\text{NaHCO}_3$ . *Di*[glycyl]leucyl]piperazine, m.  $182-4^\circ$ , from VI and alc.  $\text{NH}_3$ , and extn. with alkali and  $\text{CHCl}_3$ . *Di*[ $\alpha$ -bromopropionyl]leucyl]piperazine (VII), m.  $205^\circ$ , from V,  $\text{MeCHBrCOCl}$  and  $\text{NaHCO}_3$ . *Di*[alanyl]leucyl]piperazine, m.  $142-9^\circ$ , from VII and alc.  $\text{NH}_3$ . A. W. Dox

The influence of solvents on rotatory power (LUCAS) 2. Separation of aliphatic amines from  $\text{NH}_3$  (LEONE) 6. Magnetochemical researches on the formation of fixed chains and of nuclear groups in organic compounds (PASCAL) 2. Ultra-violet absorption spectra of dichloroethylenes (ERRERA, HENRI) 3.

SADLER, SAMUEL P. and MAYOS, LOUIS J.: *Industrial Organic Chemistry*. 5th ed. Revised. Philadelphia: J. B. Lippincott Co. 691 pp. Reviewed in *Chemicals* 24, No. 1, 11 (1923).

Catalytic oxidation of hydrocarbons. F. B. MAXTED and B. E. COKE *Brit.* 228,771, June 4, 1924. Vanadates of Sn and Bi are used as catalysts for oxidation of aromatic hydrocarbons with an O-contg. gas, e. g., in the oxidation of  $\text{C}_{10}\text{H}_8$  to produce phthalic acid and phthalic anhydride or of anthracene to produce anthraquinone. In oxidizing toluene vapor with Bi vanadate as catalyst, benzaldehyde is the main product but with Sn vanadate benzoic acid is produced.

Isopropyl chloride. G. O. CURME, JR. U. S. 1,545,742, July 14.  $\text{Me}_2\text{CHCl}$  is made by reaction of  $\text{HCl}$  on  $\text{MeCH}:\text{CH}_2$  under anhydrous conditions. Cf. C. A. 19, 523.

Concentrating alcohols, vinegar, etc. F. E. LICHTENTHALER *Brit.* 228,301, Dec. 4, 1923. See U. S. 1,492,717, C. A. 18, 2173.

Glacial acetic acid from chloroacetic acid waste liquor. W. S. CALCOTT. U. S. 1,547,201, July 28. Comminted Fe is brought into contact with a mixt. contg.  $\text{ClCH}_2\text{CO}_2\text{H}$  and  $\text{Cl}_2\text{CHCO}_2\text{H}$ , substantially free from  $\text{H}_2\text{O}$  (such as the mixt. obtained as a waste mother liquor in chloroacetic acid manuf.) in order to form Fe acetate.  $\text{HOAc}$  is regenerated from the acetate.

Sulfonating benzene. J. M. WEISS. U. S. 1,547,186, July 28. A  $\text{H}_2\text{SO}_4$  contg.

58-70% free  $\text{SO}_3$  is used for the sulfonation in order to obtain a product low in  $\text{H}_2\text{SO}_4$  and suitable for direct neutralization

**Nitrobenzoic acid.** F H BEALL and D B BRADNER U S 1,546,191, July 14 *o*-Nitrotoluene to be oxidized is treated with  $\text{HNO}_3$  until a relatively small proportion of the material treated is converted into *o*-nitrobenzoic acid A portion of the oxidation product is then sep'd., e. g. by crystn and centrifuging, and the mother liquor is retreated.

***o*-Acylbenzoic acids.** W WOLLASTON U S 1,547,280, July 28 The reaction mass resulting from the condensation of phthalic anhydride with a benzenoid compd such as  $\text{C}_6\text{H}_6$  in the presence of  $\text{AlCl}_3$  is digested with a dil inorg acid, e. g. 4%  $\text{HCl}$ , until the org Al compd present is decomposed The mixt is then allowed to sep. into a lower aq layer contg. an Al salt and an upper layer comprising a soln of benzoylbenzoic acid or other acylbenzoic acid formed in an excess of the  $\text{C}_6\text{H}_6$  or other benzenoid compd. used as starting material The layers are sep'd and the product is recovered.

**4,4'-Dihydroxy-1,1'-dinaphthyl ketone.** G DE MONTMOLLIN and J SPIELER. U. S. 1,547,102, July 21. 4,4'-Dihydroxy 1,1'-dinaphthyl ketone, nearly colorless crystals, m.  $243^\circ$ , and sol. with caustic alkalis and alkali carbonates, is made by reaction of  $\alpha$ -naphthol in an alc.  $\text{NaOH}$  soln. to which  $\text{CCl}_4$  and  $\text{Cu}$  are added

## 11—BIOLOGICAL CHEMISTRY

PAUL E HOWE

### A—GENERAL

FRANK P. UNDERHILL

**Laccase.** IV. Action of sodium chloride. Influence of the reaction of the medium. P. FLEURY. *Bull soc chim biol* 7, 188-94(1925)—See C. A. 19, 836

A T CAMERON

**Catalase.** SERGIUS MORGULIS *Ergebnisse Physiol* 23, I Abt 308-67(1924).—A review contg. a discussion on the prepn, nature, the effect of reaction on the activity, the activation and inactivation, the kinetics of the catalase reaction and its clinical application. The catalase content is not an index of the rate of metabolism On the basis of his unpublished expts M concludes that catalase is not a true oxidizing enzyme but it apparently is of value in the destruction of  $\text{H}_2\text{O}_2$ , thus preventing the accumulation of this substance which is toxic when present above a certain concn.

H. J. DEUEL, JR.

**Insulin.** Its preparation, physiological and pharmacological activity, with regard to its standardization. A. GREVENSTUK and ERNST LAQUEUR. *Ergebnisse Physiol* 23, II Abt. 1-267(1925)—An exhaustive treatise on the insulin problem with a bibliography of 600 papers.

H. J. DEUEL, JR.

**Catalysis of oxido-reductions by blood pigments.** WERNER LIPSCHITZ. *Z. physiol. Chem.* 146, 1-43(1925)—In the presence of blood pigment  $\text{NH}_2\text{OH}$  undergoes oxido-reductive decompn. at great velocity with formation of  $\text{NH}_3$ ,  $\text{N}_2$ , nitrite and nitrate, the blood pigment being converted at the same time into methemoglobin. Frog muscle, blood charcoal, bile pigment, chlorophyll, hemin and serum are incapable of transforming  $\text{NH}_2\text{OH}$  into  $\text{NH}_3$ . With  $1/2$  mol. of oxyhemoglobin as catalyst the decompn. yields  $1/2$  mol. of the  $\text{NH}_2\text{OH}$  as  $\text{NH}_3$ ,  $1/2$  as  $\text{N}_2$ , and  $1/2$  as nitrite and nitrate, thus an approx. quant. recovery. With  $1/2$  mol. of reduced hemoglobin the yields are  $1/2$   $\text{NH}_3$ ,  $1/2$   $\text{N}_2$ , and  $1/2$  nitrite and nitrate, about  $1/2$  of the  $\text{NH}_2\text{OH}$  remains unaccounted for, though small amts of  $\text{N}_2\text{O}$  were found. After absorption of  $\text{CO}$  by hemoglobin the yield of  $\text{NH}_3$  falls to  $1/2$ . Methemoglobin and  $\text{NO-Hb}$  have a catalytic action similar to that of oxyhemoglobin and  $\text{CO-Hb}$ . Absorption of  $\text{HCN}$  by the blood pigment inhibits catalysis only moderately, and in this case no color change occurs. In studying the kinetics of the reaction it was found that by 1 mol. of blood pigment 24 mol. or more of  $\text{NH}_2\text{OH}$  are decompd. with formation of  $\text{NH}_3$ , although the decompn. gradually becomes less complete. Since previous addn of reaction products has practically no influence on the catalysis and even facilitates that of methemoglobin, the retardation of the reaction is explained by decreased adsorption of  $\text{NH}_2\text{OH}$  on the hemoglobin particles. The  $\text{NH}_3$  and  $\text{N}_2$  curves resemble adsorption isotherms. Röntgen irradiation, pptn. of hemoglobin by  $\text{EtOH}$  or colloidal  $\text{Fe(OH)}_3$  do not influence the catalytic activity. When the blood pigment is split into globin and the prosthetic group by heating, the formation of  $\text{NH}_3$  drops to 10% or less. The transformation of  $\text{NH}_2\text{OH} \rightarrow$

nitrite  $\rightarrow$  nitrate is dependent on the main catalysis but is more complicated. Oxy-hemoglobin and reduced hemoglobin are different catalysts. A. W. DOX

Some considerations of protoplasm. B. FRNK. *Ohio J. Sci.* 25, 99-115(1925) — A summary and discussion of definitions for the term protoplasm offered by contemporary biologists. W. F. GOEBEL

Hydrogen-ion concentration and the oxidation-reduction potential of the cell-interior: a microchemical study. JOSEPH NEEDHAM AND DOROTHY M. NEEDHAM. *Proc. Roy. Soc. (London)* 98B, 250-86(1925) — The cell interior of *Amoeba proteus* has a hydrogen ion concn. of approx.  $pH$  7.6, and an oxidation reduction potential between  $pH$  17 and 19. JOSEPH S. HEPBURN

Recent advances in biochemistry. R. K. CANNAN. *Science Progress* 20, 26-31 (1925) — Review of recent work on the parathyroid hormone, rickets and hemoglobin. JOSEPH S. HEPBURN

Hydrogen-ion concentration and growth. W. H. PEARSELL. *Science Progress* 20, 58-67(1925). — Review of the influence of H-ion concn. upon the growth of plants and animals. Some attention is paid to isoelec. points of proteins, and the optimum reaction for enzymes. JOSEPH S. HEPBURN

Studies on proteins. VIII. The solubility of the serum globulins. S. P. L. SPØRENSEN. *Compt. rend. trav. Lab. Carlsberg* 15, No. 11, 29 pp.(1925), cf. *C. A.* 19, 1869 — Studies of the globulin content of blood serum (fractional pptn., dialysis, soly. tests, etc.) all lead to the conclusion that the globulins both in the serum itself and in the sepd. globulin fractions obtained from serum do not occur as mixts. of 2 or more globulins but as compds. of the same. These compds. of euglobulin and pseudoglobulin are easily sol. in  $H_2O$  and dil. salt solns. as long as the compds. contain a considerable quantity of pseudoglobulin, but in proportion as the latter is split off by a simple dissociation process, e. g., diln. with  $H_2O$ , the compds. of the 2 globulins become less easily sol. It is believed that there is not involved the question of transformation of one globulin to the other, but by the dissociation of the compd. of the 2, one fraction can be made by proper fractionation to yield part of the other. All the most highly purified products appeared to be easily dissociable compds. contg. both eu. and pseudo globulin, and varying in soly. according to the relative proportions of the 2 they contain. H. B. LEWIS

Proteins and the Donnan equilibrium. D. I. HITCHCOCK. *Physiol. Rev.* 4, 505-31(1925); *Ergebnisse Physiol.* 23, I Abt. 274-307(1924) — Review with bibliography. Expts. quoted indicate the amphoteric nature of proteins, their capacity to combine with acids or bases depending on whether the H ion concn. is greater or less than the isoelec. point. Donnan's theory of membrane equil. applies wherever one type of ion is present which is unable to diffuse through a membrane permeable to other ions. The theory is applied in the explanation of the action of electrolytes on membrane potentials and the osmotic pressure of protein solns., and on the swelling and viscosity of gelatin. Colloidal and crystalloidal behavior rather than colloidal and crystalloidal substances are distinguished. E. R. LONG

The identity of hematoïdin and bilirubin. A. R. RICH AND J. H. BUMSTEAD. *Bull. Johns Hopkins Hosp.* 35, 225-32(1925). — "Hematoïdin obtained from the hemorrhagic contents of a cyst of the omentum has been subjected to the phys. and chem. tests and reactions which are characteristic of bilirubin and in every instance it has behaved precisely as did a control of pure bilirubin. In this study urobilin (hydrobilirubin) has been prepd. from hematoïdin by reduction, and cholecyanin (bilicyanin) by oxidation. These are characteristic oxidation and reduction products of bilirubin. These facts are offered in support of the belief that hematoïdin and bilirubin are identical. The common statement that hematoïdin is an isomer of bilirubin rests upon no evidence of any sort." A. P. LOTHROP

The formation of sulfhemoglobin. A. A. HJMAN'S VAN DEN BERGH AND H. WIERINGA. *J. Physiol.* 59, 407-12(1925) —  $H_2S$  combines with hemoglobin or reduced hemoglobin only in the presence of  $O_2$ . The accelerating action of  $PhNHNH_2$  upon the formation of sulfhemoglobin from hemoglobin and  $H_2S$  is only observed if  $O_2$  be present. J. F. LYMAN

Electrometric measurements of cells. G. EYTSCHE AND T. PÉTERFI. *Arch. ges. Physiol. (Pflüger's)* 203, 454-66(1925) — Description of app. and technic. Electrometric studies on *Amoeba terricola*. I. *Ibid.* 467-75 — Within the limits of the method, no lack of equil. in the ions of the cell contents could be detected. In the protoplasmic colloid system water, or aq. solns. of electrolytes, undoubtedly serves as the dispersion agent. G. H. S.

The significance of the oily drops in the eggs of teleosts and the localization of

oxidases. G. BRUNELLI *Atti accad. Lincei* [6], 1, 592-4(1925) —B obtained the characteristic reaction between  $\alpha$ -naphthol and dimethyl-*p*-phenylenediamine, of oxidizing enzymes in these only drops. The localization of oxidases in teleostean eggs is discussed. E. J. WITZEMANN

The spontaneous decomposition of lecithin. SHICHIZO KATO and OSAMU SHINODA, *Mem. Coll. Sci. Kyoto Imp. Univ.* 7A, No. 5, 339-43(1924) —Pure ovo-lecithin from Merck (after keeping 8 yrs.) was analyzed and found to be a mixt. of pure lecithin and cephalin giving C, 59.61%, H, 11.80%, N, 7.82%, P 3.58% with N:P = 1.06, while pure lecithin has approx. the compn. C, 64.63%, H, 10.96%, N, 2.08%, P, 3.97%, with N:P = 1:1.16. 20 g. of the sample were dissolved in Et<sub>2</sub>O, concd. to small vol., poured into dry Me<sub>2</sub>CO, the ppt. was sepd., dried *in vacuo* and redissolved in Et<sub>2</sub>O. After reprecip. 3 times, analysis gave C, 50.88%, H, 10.35%, N, 1.53%, P, 5.28%, with N:P = 1:1.4, showing that some of the fatty acids had been removed. Hydrolysis by alc. NaOH and fractional pptn. of the Mg salts in 98% EtOH (*J. prakt. Chem.* 66, 12(1855)) did not resolve it into palmitic and stearic acids. The Me<sub>2</sub>CO soln. from the above pptn. was concd., dissolved in Et<sub>2</sub>O, NH<sub>3</sub> passed in and the salts were converted part to the Ca and part to the Pb salt. The acid from the Ca salt in 52-53° and gave C, 73.13%, H, 12.96% and mol. wt. 270. The acid from the Pb salt in 52-53° and gave C, 73.13%, H, 12.88% and mol. wt. 272, indicating a mixt. of palmitic and stearic acids. A 2nd sample of Merck's lecithin, though having nearly the correct compn. after purification by the above method was similarly shown to have largely decompd. into a mixt. of palmitic and stearic acids and a residue rich in P and N. M. A. YOURTZ

HACROWITZ, F.: *Biochemie des Menschen und der Tiere seit 1914. Part XII.* Edited by R. E. Liesegang. Wissenschaftliche Forschungsberichte. Dresden and Leipzig. T. Steinkopff. 148 pp. Paper, M. 7, bound, M. 8.20

PEABODY, J. E. and HUNT, A. E. *Biology and Human Welfare.* New York: Macmillan Co. 585 pp. \$1.68. Reviewed in *J. Chem. Education* 2, 621(1925)

Some Studies in Biochemistry. By some Students of Dr G. J. Fowler. Bangalore: Phoenix Printing House. 197 pp. Reviewed in *Chemistry and Industry* 44, 687(1925).

## B—METHODS AND APPARATUS

STANLEY R. BENEDICT

Detection of sugars by means of Nylander's reagent. O. ASCHAN *Soc. Sci. Fennica Commentationes Phys.-Math.* 2, No. 8, 1-11(1924) —Since little is known of the reduction effects of saccharides other than glucose on Nylander's reagent, and since other saccharides (pentoses, disaccharides, etc.) often appear in the urine under abnormal conditions, a systematic study of the behavior of pentoses (arabinose, xylose, rhamnose), hexoses (glucose, fructose, galactose), disaccharides (sucrose, lactose, maltose), and polysaccharides (starch, dextrin, lichenin), toward this reagent was made. Nylander's reagent was readily reduced by all of the above saccharides except sucrose, starch and lichenin. When the test was carried out in fresh urine instead of water soln., a heavier ppt. was obtained. This increase was probably due to the formation of insol. inorg. material. Both glucose and fructose can be detected in concns. as low as 0.06%. Since neither HCHO, MeCHO nor PhCHO gives a typical reduction test, it is concluded that only  $\alpha$ -hydroxy-aldehydes or ketones react with Nylander's reagent. W. F. GOEBEL

Stools in infancy. EARL M. TARR *Arch. Pediatrics* 42, 404-10(1925) —A description of the various types of stool, and of methods for their examn. J. S. H.

Why dental instruments rust and how to prevent it. W. S. CROWELL. *Dental Cosmos* 67, 752-5(1925) —The chief cause of rusting is sterilization. Rusting may be minimized by addition of Na<sub>2</sub>CO<sub>3</sub> and NaNO<sub>2</sub> to the water in the sterilizer. JOSEPH S. HEPBURN

The imponderables. I. S. KLEINER *J. Am. Inst. Homeopathy* 18, 681-5(1925) —A study of the limit of sensitivity of tests for inorg. ions, of the senses of taste and smell, and of biol. tests for vitamins, hormones, bacterial toxins and anaphylaxis. These tests detect the presence of the solute frequently in the 10th diln. on the decimal scale, occasionally at higher dilns., e. g., the 18th. A concn. of 1 mol. per cc. is usually attained at approx. the 23rd diln. on the decimal scale. JOSEPH S. HEPBURN

A simple method for studying the oxygen consumption and other vital manifestations of tissue. J. DE HAAN. *Arch. néerland. physiol.* 9, 272-6(1924) —Equal quantities of leucocytes taken from the abdominal cavity of rabbits were suspended in 0.9% NaCl satd. with atm. air; ultrafiltered beef serum satd. with atm. air; and ultrafiltered

beef serum satd. with atm. air contg. 6-7%  $\text{CO}_2$ . The liquids were placed in glass ampoules with capillary openings. Samples were removed at various intervals and the gaseous tensions detd. by the method of Krogh. The presence of the  $\text{CO}_2$  stimulated the utilization of the  $\text{O}_2$ . The increase in H-ion concn. of the solns. was due to the formation of lactic acid rather than to respiratory  $\text{CO}_2$ . The solns. remained sterile throughout the expts. An adaptation of the method to organ and tissue respiration was indicated but no data are given. M. H. SOULE.

New tests for cystine and cysteine. M. X. SULLIVAN *Abstracts Bact* 9, 37 (1925), cf. C. A. 18, 3614.—Of many amino acids and S and sulphydryl compds. cysteine is the only one that gives a red color with Na  $\beta$  naphthoquinone-4-sulfonate in the presence of alkali and a reducing agent such as  $\text{Na}_2\text{SO}_3$ . Cystine gives the reaction slowly by reason of gradual reduction of the cysteine by the sulfite. If NaCN be added to a cystine soln., before addn. of the naphthoquinone and sulfite, the characteristic color reaction for cysteine is obtained because the cyanide reduces the cystine to cysteine. S. applied these reactions to det. differences in peptones. F. W. TANNER.

## C—BACTERIOLOGY

A. K. BAILS

The fermenting power of fresh yeast toward galactose induced by preliminary treatment and the persistence of this property. HANS V. EULER AND THOR LÖVGREN *Z. physiol. Chem.* 146, 44-62 (1925).—By preliminary treatment with galactose the power of fermenting this sugar was developed in top yeast R from the local distillery. With the adaptation to galactose the fermenting power of the yeast toward glucose diminished in the proportion of 55:30. The capacity of fermenting galactose never reached 50% of the glucose-fermenting power. After this preliminary treatment (adaptation) the yeast was again cultivated in its natural medium, glucose, but even though the latter treatment exceeded in duration (282 hrs.) the period of adaptation, a loss of the acquired galactose fermenting power did not result, but on the contrary the galactose-fermenting power continued to develop. A. W. DOX.

Studies on *B. pestis*. I. Optimum and limiting hydrogen ion concentration for the growth of *B. pestis*. RIGNEY D'AUNOY. *J. Infectious Diseases* 33, 391-415 (1923).—In this study a detn. of the range of growth and optimum requirement of *B. pestis* on the basis of the newer concepts of reaction standards has been undertaken. The growth range of stock cultures of *B. pestis* is from  $p_H$  5.0 to 8.2, the optimum growth being at  $p_H$  6.2 to 7.0. Organisms recovered from a fatal infection in white rats showed a growth range from  $p_H$  5.4 to 7.6, with optimum growth at  $p_H$  6.0 to 6.6. The minimum concn. of dextrose needed by *B. pestis* to give its final characteristic H ion concn. is intimately dependent on the initial reaction of the medium employed. With an initial reaction of  $p_H$  6.8 a dextrose concn. of at least 0.5% is necessary for the establishment of the final characteristic H ion concn. of  $p_H$  4.8. Tests with a large no. of carbohydrates show that fermentation as a basis of classifying of *B. pestis* is of no value. Suspensions of *B. pestis* in NaCl soln.,  $p_H$  6.8, were stable for a long time. Killed organisms injected in various ways over long periods of time gave indifferent results, but organisms attenuated by growing in alc. broth and finally fully virulent organisms when injected into animals produced serums with an agglutimative titer of 1:600 to 1:15,000. Serums obtained from cases of plague showed irregular bacteriolytic action on *B. pestis* which could not be demonstrated 10 and 14 mos. after recovery. The bacteriolytic substance is thermolabile and seems to consist of 2 parts, alexin and another destroyed by heat at 68°, and is not demonstrable in the  $\text{CO}_2$  precipitable globulin. Protective antiplague serums showed no bacteriolytic action. Normal serums contained no bactericidal or bacteriolytic substance. JULIAN H. LEWIS.

The inhibition of putrefactive spore-bearing anaerobes by *Bacterium acidophilus*. J. C. TORREY AND M. C. KAHN. *J. Infectious Diseases* 33, 482-97 (1923).—The ability of *B. acidophilus* and *B. bifidus* to overgrow and suppress in the intestines the types of bacteria usually dominant there is analyzed by test-tube expts. by growing *B. acidophilus* with several varieties of proteolytic spore-bearing anaerobes. The inhibition of these proteolytic anaerobes by *B. acidophilus* seemed to be entirely dependent on the acid produced by the latter. There seems to be no great difference between *B. acidophilus* and *B. coli* in their inhibitive action. Lactic acid was found to exercise a somewhat greater inhibitory effect on proteolysis by *B. sporogenes* than does HCl. No inhibitory product, other than acidity, for these spore-bearing anaerobes, could be detected in the fluid cultures of *B. acidophilus*. JULIAN H. LEWIS.

Theory of electrical conductance of suspensions. F. H. McDUGALL AND R. G.

GREEN. *J. Infectious Diseases* 34, 192-202(1924).—Theoretical consideration is given to an inhomogeneous suspension as a system of resistances. The derivation of formula is presented leading to expressions by means of which the sp. resistances of suspended cells and their fractional vol. of the suspension may be calculated. The sp. resistance of live *B. coli* is about 1000 ohms and the sp. resistance of *S. cerevisiae* about 4,000 ohms. After death by heat the sp. resistance of *B. coli* is increased and that of *S. cerevisiae* is decreased. On death by heating the vol. of bacterial and yeast cells as determined by calculation decreases.

JULIAN H. LEWIS

Study of the cultural requirements of *Spirochaeta pallida*. CHARLES WEISS AND DOROTHY WILKES-WEISS. *J. Infectious Diseases* 34, 212-26(1924).—More than 40 media of other authors as well as a few of these authors' own compositions were selected and modified to conform to some of the physicochemical requirements possessed by Noguchi's ascites-kidney-agar medium in order to find some medium which could be obtainable with less difficulty for the culture of *Spirochaeta pallida*. The following gave good growth at optimum reaction  $pH$  7.6-7.8 and under a petrolatum seal; whole egg added to "hormone" broth (1:4) heated for 1 1/2 hr. in an Arnold sterilizer, the authors' whole egg broth; modified Kligler's medium (with freshly obtained rabbit blood), unheated and heated horse serum broth. These media are greatly improved by the incorporation of 0.2% agar.

JULIAN H. LEWIS

Oxidase activity and isolation of pure cultures of bacteria. L. D. FELTON. *J. Infectious Diseases* 34, 407-13(1924).—A 1:5000 dilution of *p*-aminoleucomalachite green in a 0.5-1.0% dextrose whole blood meat infusion agar with a  $pH$  of 7-7.6 will show the presence of oxidase in bacteria by the production of faint blue colonies. As pneumococci and streptococci are the only bacteria which consistently cause oxidation of this indicator, the medium offers a practical method of isolating pure cultures of these organisms.

JULIAN H. LEWIS

A new indicator for testing reducing power of bacteria. L. D. FELTON. *J. Infectious Diseases* 34, 414-9(1924).—Certain organisms change the green dye, *p*-nitro-malachite green, to the red one, *p*-aminomalachite green. Of 13 different bacterial species grown in plain broth with the dye in a concentration of 1:10,000 all gave a positive reaction except *B. alkaligenes*, *B. diphtheriae*, and pneumococci. In 10% horse serum, *B. typhosus* and meningococci were the only species studied which gave a pronounced reaction. *Staphylococcus aureus* and *albus* and *Streptococcus hemolyticus* gave a slight reaction in plain broth and in horse serum. *B. coli* caused a marked reduction in plain broth but only a slight reaction in the serum.

JULIAN H. LEWIS

Studies on respiratory diseases. XIX. Untreated bile as a solvent for pneumococci. F. B. KELLY AND HARRY GUSSIN. *J. Infectious Diseases* 35, 327-33(1925).—Stored, untreated whole ox bile dissolves pneumococci better than the bile prepared ordinarily used. It dissolves dextrose broth cultures readily with no interference from peptone.

JULIAN H. LEWIS

Green coloration by certain streptococci on blood agar. W. A. HAGAN. *J. Infectious Diseases* 37, 1-12(1925).—The green discoloration of blood agar by streptococci and other bacteria is due to the combined action of peroxide and acid which are produced by these bacteria. When acid alone is produced or when the peroxide is exhausted, hemolysis alone is produced. It is assumed that methemoglobin is concerned in the process of production of the green color, although it is unlikely that this substance is the cause of the color as methemoglobin is brown instead of green.

J. H. L.

Proliferative reaction to stumby by the lytic principle (bacteriophage) and its significance. PHILIP HADLEY. *J. Infectious Diseases* 37, 35-48(1925).—Abnormally rapid growth is frequently observed in bacterial colonies under the influence of bacteriophage. This is analogous to the observation made by d'Herelle that the primary reaction made to any ultravirus is a proliferative process.

JULIAN H. LEWIS

Microbes and vitamins. P. GOY. *Ann. inst. Pasteur* 39, 183-93(1925).—In cultures of *Amylomyces*  $\beta$  (Delema) there is a substance which promotes the growth of yeast and bacteria in general. It is not identical with vitamin B. It resists 130° for 1.5 hr.

E. R. LONG

The carbon of peptone as a source of energy for the diphtheria bacillus. G. ABR. *Ann. inst. Pasteur* 39, 387-416(1925).—The diphtheria bacillus in Martin's bouillon produces about 4 g.  $CO_2$  for 1100 cc. medium and 1.1 g. dry bacilli. About 80% is formed in the first 10 or 12 days of culture and 95% in the first 20 days. Bacterial activity is maximal in the first 2 days, when the reaction is slightly alk. The production of  $CO_2$  is an exact measure of the activity of the bacillus, and permits an evaluation of the nutritive capacity of a medium. In Martin's bouillon, which contains no sugar, the  $CO_2$  is derived about 1/3 from organic acids present and 2/3 from protein substances.

The fatty acids form an intermediary stage between the amino acids and  $\text{CO}_2$ .  $\text{AcOH}$  and  $\text{BuOH}$  are more easily burned than  $\text{HCOOH}$  and valeric acid. Glutamic acid is especially well utilized. The heat of combustion in the microbial bodies represents 30% of the total heat liberated in the system. The  $\text{O}_2$  requirement is more than 21 per culture flask. The coeff. of protein utilization in Martin's bouillon does not pass 10%. Of the amino acids appearing in the medium in the course of the growth only  $1/4$  are deaminized and consumed.  $\text{NH}_3$  is liberated. Certain nitrogenous principles are quite indispensable but a greater amt. of substance quant. is necessary for the production of the energy necessary for the maintenance of life. E. R. LONG

Action in vitro of certain substances on the development of tubercle bacilli. LEON KARWACKI AND STANISLAS BIERNACKI *Ann. Inst. Pasteur* 39, 476-83 (1925).—The action of various substances was tried on a rapidly grown strain of tubercle bacillus, which was acid fast, but practically devoid of virulence. Guaiacol and guaiacetic acid are inactive in 0.1% concn., or the equiv. of a dose of 60 g for a 60-kg subject. The value of this substance in tuberculosis therapy therefore is not due to its bactericidal power. Urotropine arrests the growth of the bacilli only in a concn. equiv. to 8 g per l. urine per day. Colloidal As is bacteriostatic at 0.002-0.01%, arsenous acid at 0.02%. Org. As preps are of feeble activity. Ag albuminate retards growth at 0.08%. Zn is one of the few metals which in the colloidal state retard growth. Most dyes are inactive, but pyronine, alizarin and cyanine have an appreciable effect. Among the most effective bacteriostatic agents were cyanide of Au and K, oxycyanide of Hg, colloidal As, thioflavin and methylene blue. E. R. LONG

The alleged power of bacteria to form bile pigment from hemoglobin. A. R. RICH AND J. H. BUMSTEAD *Bull. Johns Hopkins Hosp.* 36, 376-80 (1925); cf C. A. 19, 1005.—No bilirubin is formed in amts. detectable by the van den Bergh or Gmelin's tests or by extn. with warm  $\text{CHCl}_3$  when whole or laked blood or solns. of hemoglobin are subjected to the action of *Pneumococcus*, *Staphylococcus aureus*, *Streptococcus viridans* and air bacteria. Gmelin's test gives an atypical green ring and this atypical reaction may have played a role in the conclusions of previous investigators who have claimed that bilirubin can be readily formed by bacterial action. The formation of bile pigment from hemoglobin by the action of enzymes. *Ibid.* 437-45.—"The assumption is frequently made that there is present in the body an extracellular enzyme having the power to convert hemoglobin into bile pigment. We have been unable to demonstrate an enzyme of this nature in the plasma or in the spleen in expts. conducted under conditions ordinarily favorable to enzyme action. Contrary to statements in the literature, bilirubin was never formed in our expts. when hemoglobin was subjected to the action of trypsin." A. P. LOTHROP

Hydrolysis of inulin by means of microorganisms. JEAN DECLERCK. *Bull. assoc. éco. sup. brasserie Louvain* 25, 160-6 (1925).—Tests carried out at 25° with a large no. of organisms on Raulin's medium in which sucrose was replaced by 2.5-5 g. per l. of inulin showed that the organisms hydrolyze the inulin to levulose before assimilating it, and when the rate of hydrolysis is low the levulose is assimilated practically as rapidly as it is formed. *Aspergillus niger* was the most active, and *Bacillus mesentericus*, *Sterigmatocystis alba*, *Trichothecium roseum*, *Penicillium griseo-roseum*, *Phycomyces heterosporus* and *Fusarium hordei* also hydrolyzed it well. The others gave slight or no hydrolysis. A. PAFINEAU-COUTURE

Hydrogen peroxide and bacterial growth. P. M. BURNET. *Australian J. Exptl. Biol. Med. Sci.* 2, 11, 65-76 (1925).—Exposure of nutrient agar plates to light results in the appearance of traces of  $\text{H}_2\text{O}_2$  sufficient to inhibit the growth of isolated staphylococci and other organisms. This inhibition can be neutralized by diffusible products of growth of staphylococci. These diffusible substances, some of which are thermostable, act as reducing agents and destroy any  $\text{H}_2\text{O}_2$  as it is formed. An inhibition of growth due to KCN can also be neutralized by these substances. Anaerobic growth of staphylococci is possible in concns. of cyanide higher than those completely inhibiting aerobic development. Apparently the presence of catalase and of the diffusible substances studied in the bacterial colony is an indication of a primitive means of keeping const. the immediate environment, so as to allow the type of metabolism most suited to the organism to be maintained. Effect of dyes on bacterial growth. *Ibid.* 77-82; cf Churchman, C. A. 17, 788, 1818, 2726, 3354, 3373.—Attention is called to the fact that Gram-positive bacteria are in general more sensitive to disinfecting agents than are Gram-negative bacteria, also that the results obtained with Gram positive spore bearers toward dyes, of which acid lichen is a representative, are remarkably parallel to those obtained from similar bacteria toward  $\text{H}_2\text{O}_2$ . Several theories are suggested to account for this parallelism. L. W. RIGGS

Acid-forming bacteria in deep dental canes. I. HEIM *Arch Hyg* 95, 154-9 (1925).—A review of the literature and a report of 18 cases F. B. SEIBERT

Some observations on Eudo's medium. N. M. HARRIS *Abstracts Bact* 9, 3 (1925).—To ascertain the factors of instability in this medium, H followed the technic set by the Committee on Standards of the A. P. H. A., testing 4 samples of dyes and 4 samples of peptones. Levine's formula also was used. The incorporation of meat ext. in most of the combinations was one factor giving rise to unsatisfactory results. Basic fuchsin which contained a mixt. of a rosaniline and pararosaniline gave more consistent results than did samples of basic fuchsin contg chiefly rosaniline ("new fuchsin"). Best results were obtained when the  $pH$  lay within the limits of 7.4 to 7.8. In Levine's formula Witte's peptone gave much poorer results than did 3 samples of American peptones. A  $Na_2SO_4$  content of 0.25% was much more advantageous than one contg 0.125%. Sensitivity of the medium to light, in most cases, depends upon the kind of dye used, the most stable being a dye contg a mixt of pararosaniline and rosaniline, in lesser degree upon the peptone; and plates with a sulfite content of 0.125% were more susceptible to light than those contg 0.25% F. W. TANNER

A study of the nitrogen content in volumetrically standardized bacterial vaccines. RUTH KAUTSKY, FRANZ LEINWEBER AND L. W. FANULENER *Abstracts Bact* 9, 6 (1925).—The total N content was detd in 10 volumetrically standardized vaccines representing the 3 chief morphological types of organisms, *B. coli communis*, *Staphylococcus aureus* and *Streptococcus viridans*. The N content of members of the same species corresponded fairly closely. However, in each series, one or more members did not closely conform to the av. nitrogen content as shown by others of the group. The irregularities probably were due to error of construction, or in calibration of the centrifuge tube used in collecting and measuring the bacterial substance. Further studies are in progress to det. the possible sources of error, as revealed by the preliminary detns and their elimination from the method. By means of the volumetric method of standardization of vaccines, simplicity of technic, rapidity of procedure and possible accuracy of results are promised. F. W. TANNER

Further studies on cataphoresis [of bacteria]. C. E. A. WINSLOW, H. J. SHAUGHNESSY, E. H. FLEESON AND M. F. UPTON *Abstracts Bact* 9, 7 (1925) F. W. T

The possibilities of the conductivity method as applied to studies of bacterial metabolism. L. B. PARSONS AND W. S. STURGES *Abstracts Bact* 9, 10 (1925).—Results are given of a study of cond. changes in bacterial proteolysis as related to formol titration and  $NH_3$  changes. Eight different strains of *Clostridium sporogenes* and *Cl. flabelliferum* were studied in nutrient gelatin while two strains each were studied in milk and nutrient broth. Within 10% the cond change was proportional to the ammonia change. Formol titration changes followed cond changes closely F. W. TANNER

The magnitude of the error due to ammonia and its salts in the Van Slyke procedure for amino nitrogen as commonly applied in studies of bacterial metabolism. L. B. PARSONS AND W. S. STURGES *Abstracts Bact* 9, 11 (1925).—A quant study, from the physico-chemical point of view, has been made of the decompn of  $NH_4$  salts in the Van Slyke procedure. The reaction is of the first order. This leads to the conclusion that the relative amts. of  $NH_3$  N evolved are independent of the initial concns. of the  $NH_4$  salts. This was demonstrated experimentally over the range of 100-500 mg. of  $NH_3$  N per 100 cc. The reaction has a temp coeff of 3.0 at 20-30°. The results adequately account for the failure of some investigators to obtain satisfactory checks. F. W. TANNER

Indicators of anaerobiosis. W. M. CLARK AND B. COHEN *Abstracts Bact* 9, 12 (1925).—Quant data for equil. conditions in the reversible oxidation-reduction of methylene blue show that the theoretical O tension at the equil. state should be so small as to be of no physical significance. The same is true of several other indicators used in bacteriological studies. Therefore, they cannot be used to establish partial O tensions of any significance. Since indophenols are reduced by living cells their reductive processes are intense. Indicators mentioned can be used to det. reduction intensities and values for these were established in terms of electrode potentials. True anaerobic processes must henceforth be treated without any reference to partial tensions and, at least for convenience, in terms of reductive intensities expressed as potentials F. W. TANNER

Fermentation characteristics of mannitol-forming bacteria. W. H. PETERSON, P. B. FRED AND H. R. STILES. *Abstracts Bact* 9, 30 (1925).—Five groups of mannitol-forming bacteria have been isolated from soil, manure, water, silage, sauerkraut, yeast and cereal infusions. The fermentability of various sugars, alcs. and org acids have been detd. as a means of classifying these organisms. Arabinose, xylose, fructose, lac-

tose and raffinose proved to be the most useful in differentiating the several groups. The chief fermentation products are acetic acid and lactic acid from pentoses; ethyl alc., lactic acid and  $\text{CO}_2$  from the aldohexoses; acetic acid, lactic acid,  $\text{CO}_2$  and mannitol from fructose. From 90 to 95% of the sugar fermented was accounted for by these products. With fructose the fermentation was particularly rapid. Within 3 or 4 days after inoculation, the sugar has entirely disappeared and 50-60% of it has been converted into mannitol. The lactic acid was mainly inactive but a slight excess of one form was invariably present. With some groups, the levo and with others the dextro enantiomorph was predominant.

F. W. TANNER

**Production of gelatinase by proteus.** W. M. CLARK AND ALICE T. MERRILL. *Abstracts Bact* 9, 37(1925).—A method previously proposed was studied in greater detail and was found sufficiently quant for estg. the influence of various conditions on gelatinase formation. By means of this method it was shown that surface exposure of cultures of proteus very considerably increased the amt. of gelatinase formed in a unit time.

F. W. TANNER

## D—BOTANY

B. M. DUGGAR

**Influence of temperature on the pectinase production of different species of Rhizopus.** J. L. WEINER AND L. L. HARTER. *Am J Botany* 10, 127-32(1923).—Several species of *Rhizopus* produce decaying of sweet potatoes by production of an enzyme which dissolves the middle lamellae from the cells, whereby they lose their coherence. The potatoes are reduced to a soft watery mass, although the cells themselves, in the early stages, at least, are not penetrated. Expts with 9 species of *Rhizopus* at varying temps. indicate that pectinase is produced at any temp. at which the fungi will grow. The highest temp. gives lowest enzyme production. The different species give widely differing enzyme production.

M. S. ANDERSON

**Pectinase in the spores of Rhizopus.** J. L. WEINER AND L. L. HARTER. *Am J Botany* 10, 167-9(1923).—Spores of *R. nigricans* and *R. tritici* both contain pectinase, an enzyme capable of dissolving the middle lamellae of raw sweet potatoes.

M. S. ANDERSON

**The relation of the enzyme pectinase to infection of sweet potatoes by Rhizopus.** L. L. HARTER AND J. L. WEINER. *Am J Botany* 10, 245-58(1923).—*Rhizopus* cannot infect sweet potatoes through unbroken skin, but if given a saprophytic start infection takes place readily. Growing organisms produce an enzyme which, if evapn. is prevented, will soon dissolve lamellae of well tubers and produce infection.

M. S. ANDERSON

**Pigments of the Florideae.** G. ROBIN. *Atti accad. Lincei* [vi], 1, 188-90(1925).—Investigations on various *Florideae* of the Gulf of Naples show that the red pigment, phycoerythrin, may be crystd. from its solns. in hexagonal prisms or tablets by addn. of  $(\text{NH}_4)_2\text{SO}_4$ . It exhibits 3 absorption bands in the green, these occupying slightly different positions with different species. Phycoerythrin accompanies phycoerythrin in a few forms and possesses analogous phys. characters but exhibits only 1 or 2 bands, in the orange red region. Contrary to common opinion, phycoerythrin appears to take part in photosynthesis.

B. C. A.

**Energy of growth.** IV. The energy yield of different carbohydrates in the growth of higher plants. E. F. TEKROINE, MISS S. TRAUTMANN, R. BONNET AND R. JACQUOT. *Bull. soc. chim. biol* 7, 461-73(1925), cf. *C. A.* 19, 2226, 2346.—*Arachis* plantules sepd. from cotyledons and grown in a medium contg. certain sugars as sole org. nutrient grow well, showing that their organic C can be derived indifferently from fats or carbohydrates. Arabinose, xylose, galactose and lactose permit no growth. Growth is equal at the expense of glucose, fructose, maltose and sucrose. The energy growth for glucose averages 67%, much greater than the 53% derived from the fat reserves of the seed, and approaching the 73% for germination of seeds with purely starch reserves.

A. T. CAMERON

**Extraction and properties of gein, a glucosidal generator of eugenol, present in Geum urbanum L.** H. HÉRISSEY AND J. CHELMOL. *Bull. soc. chim. biol* 7, 499-507(1925).—See *C. A.* 19, 1442.

A. T. CAMERON

**The preparation and the properties of monotropitoxide.** M. BRIDEL AND P. PICARD. *Compt. rend* 180, 1854-6(1925).—Although the quantity of monotropitoxide in French plants is very small, 3 g. per kg. was extd. from the fresh bark of *Betula lenta* L. (American) by the method used when it was first discovered (cf. Bridel, *C. A.* 18, 703). It was purified by crystn. from  $\text{Me}_2\text{CO}$  and then from  $\text{H}_2\text{O}$ . From  $\text{H}_2\text{O}$  it

gave prisms up to 0.5 cm long contg 3.84%  $H_2O$  (theoretical 3.87%), which was evolved at  $105^\circ$ , m  $179.5^\circ$ ,  $\alpha_D -58.22^\circ$ . From  $Me_2CO$   $\alpha_D$  was  $-58.80^\circ$  and from 95% EtOH it was  $-59.25^\circ$ . At  $18.2^\circ$  1 g. of anhydrous monotropitoside dissolved in 12.361 g. of  $H_2O$ , in 150.330 g. of 95% EtOH, in 581.395 g. of EtOAc, in 649.350 g. of  $Me_2CO$  and in 1369.830 g. of  $Et_2O$ . In powdered form it gave a rose color with concd  $H_2SO_4$  with an odor of Me salicylate. The sapon no. of the methyl ester constituent was 86.7% (theoretical 86.2) with cold KOH. Fermentation hydrolysis gave primeverose (cf. Bridel, C. A. 19, 842). The glucoside constituent was not attacked by KOH at  $105^\circ$ , the liquid remaining levogyrotory. Detn. of free salicylic acid by the method of Bougault (C. A. 2, 3262) indicated only 2% hydrolysis. To det. the % salicylic acid, monotropitoside had to be first hydrolyzed with  $H_2SO_4$ , with subsequent sapon. of the Me salicylate. Analysis showed it to be  $C_{14}H_{16}O_5$ , and to be composed of 1 mol. each of Me salicylate, glucose and xylose and 2 mols. of  $H_2O$ . Its enzymolitic no. was 350, its acid no. 415.

C. C. DAVIS

Studies on two storage-rot fungi of rice. ICHIRO MIYAKE AND KAZUO TANAKA. *Rept. Imp. Cent. Agric. Expt. Sta. Tokyo* 45, 71-232 (1922); *Botan. Abstracts* 14, 87.—The change of the percentage of the chief constituents of rice in consequence of the rot is as follows (80 days culture, + increase, — decrease) for *Aspidia* and *Penicillium*, resp. water + 35.756, + 43.635, crude protein —8.61 —34.40, protein —24.73, —41.63, amides —31.70, —4.23; crude fat —2.08, —13.57, crude fiber + 194.12, + 410.78, starch (detd. by Bertrand's method) —52.25, —90.11, N-free ext. —13.35, —82.96. The authors have also described various physiological phenomena, such as the influence of various substances towards spore germination, the nutrients and their concentration, the enzymes, the behavior of the fungi towards the supply of  $O_2$ , temperature, light and various substances, the acidity of the infected rice, its toxicity for animals, etc. One type of rot is caused by a species of *Aspidia* and the other by *Penicillium commune* Thom.

H. G.

The chemistry of the date. A. E. VINSON. *Rept. 1st Date Growers' Inst., Coachella Valley Farm, Center, Coachella, Calif.* 1924, 11-2; *Botan. Abstracts* 14, 61.—Two chem. varieties of dates exist, the invert and the cane sugar types. Most of the tannin of the date is deposited as insol. grains in a zone of tannin cells near the cuticle. Premature ripening may be induced commercially by  $CO_2$  or by killing the protoplasm with heat. The keeping quality may be improved, insects and their eggs destroyed, and the palatability improved by pasteurization.

H. G.

Relative effects of some common ions on hydration, absorption and permeability. D. T. MACDOUGAL. *Carnegie Inst. Washington Year Book* 22, 50-1 (1924); *Botan. Abstracts* 14, 111.—A summary suggests that "the action of the common salts of the soil on plants is in the main detd. by the ionic mobility of the particles, with modifications due to the varying compn. of the living material and with interferences."

H. G.

Continuation of investigations on permeability in cells. W. J. V. OSTERHOUT. *Carnegie Inst. Washington Year Book* 22, 290 (1924); *Botan. Abstracts* 14, 111.—Studies are reported on entrance and exit of salts, with *Nitella* as exptl. material.

H. G.

Effect of salt solutions on hydration and swelling of plant tissues. F. T. McLEAN. *Carnegie Inst. Washington Year Book* 22, 47-9 (1924); *Botan. Abstracts* 14, 111.—Studies are reported on the swelling of stem tips of walnut and blackberry when placed in salt solutions.

H. G.

The absorption of carbon dioxide by leaf material. H. A. SPOHR AND J. M. MCGEE. *Carnegie Inst. Washington Year Book* 22, 53 (1924); *Botan. Abstracts* 14, 115.—Killed leaves are capable of absorbing  $CO_2$  in quantities above the amt. that would dissolve in the  $H_2O$  of the leaf; this study deals with the nature of the absorbing substances that are involved.

H. G.

Anthocyanin formation in *Helianthus annuus*. C. E. SANDO. *J. Biol. Chem.* 64, 71-4 (1925).—From the corollas of 3300 heads of the orange double chrysanthemum-flowered sunflower, there were isolated 20.5 g. pure *quercimeritrin*, previously isolated from cotton flowers. It is believed that the red sunflowers contain this glucoside and an enzyme which reduces it to the anthocyanin.

I. GREENWALD

Recent advances in science—Plant physiology. WALTER STILES. *Science Progress* 20, 44-9 (1925).—Review of recent work on irritability and movement in plants.

JOSEPH S. HEPBURN

Plant incrustants. VI. ERICH SCHMIDT, WALTER HAAG, JOSEPH ABELE AND LEONIE SPERLING. *Ber.* 58B, 1394-1403 (1925); cf. C. A. 16, 273; 17, 1822; 18, 1388.—The result of the oxidation of hemp and flax incrustants with 8%  $ClO_2$  and subsequent treatment with  $Na_2SO_3$  make it probable that the incrustants are esters of a phenolic substance and polysaccharides. The  $CO_2H$  for the esterification is furnished by galac-

turonic acid. Glucosides of the two constituents very likely form part of the incrustants. Evidence is furnished in support of this hypothesis. The phenolic nature of lignin is suggested by the formation of pyrocatechol and protocatechuic acids by the alkali fusion of ligninsulfonic acid and lignin-HCl. Furthermore, oxalic and maleic acids are formed by the oxidation of both, phenols and incrustants by  $\text{ClO}_2$ . On the other hand the presence of galacturonic acid in the non-oxidized incrustant must be accepted in view of the fact that  $\text{ClO}_2$  has no influence on carbohydrates and that the originally neutral incrustant turns acid when treated with hot water. The hydrolysis takes place to a larger extent in presence of alkali with salt formation.  $\text{Na}_2\text{SO}_3$  has the same effect. The acid content of the original incrustant is equal to that found in the polysaccharide fraction of the oxidation product, another proof against its being formed by oxidation. There seems to be an analogy between incrustant and skeletal substance insofar as both are esters of alcohols and hemicelluloses. In the skeletal substance cellulose and chitin play the role of the alcohols, while glucuronic acid furnishes the  $\text{CO}_2\text{H}$  group. The esters of the skeletal substance are, however, more resistant to hydrolysis. The differentiation of cell membranes into  $\text{H}_1$ , incrustant hemicelluloses, and  $\text{H}_2$ , skeletal hemicelluloses should replace the old one. The present definition of incrustants as substances resisting HCl (d 121) is also untenable, since it applies to wood lignin only. The definition, "substance attacked by  $\text{ClO}_2$ ," covers all incrustants. M. J.

The absorption of iron by plants outside of their root system. M. I. SIDOROV. *Zhurnal prikladn. agron.* 23, 3-26(1925).—Sols of  $\text{Fe}(\text{NO}_3)_3$ , 1:10,000 to 1:100,000 when applied in the form of drops on young chlorotic leaves showed that concns lower than 1:50,000 (1:216,000 in terms of Fe) were not effective in preventing chlorosis; higher concns were effective. Expts with peas and buckwheat showed that leaves are capable of absorbing iron when applied either in the form of a dip, sprinkling or drops. The time period of dip varied from 3 to 16 hrs. Within 26 days the plants were dipped 5 times. The Fe intake by the leaves was not so efficient as through the roots. With corn introduction of Fe into the stem also prevented chlorosis, although the absorption is not so good as through the roots. Chlorosis due to excess of Mg or Ca carbonates was slightly improved by introducing dil. solutions of citric acid into the stems. Especially was the greening noticeable along the veins of the upper leaves. Soaking seed corn in Fe sols helped to prevent chlorosis. J. S. JOFFE

The chemistry of Japanese plants. IV. Saturated fatty acids in camphor seed fat (*Laurus camphora* Nees). SHIGERU KOMATSU AND SEIICHI YAMADA. *Mem. Coll. Sci. Kyoto Imp. Univ.* 8A, 253-6(1925); cf. C. A. 19, 2064.—Capric acid was found abundantly in the camphor seed fat as a glyceride together with lauric acid. VII. The phytochemical study of the Yamamomo-fruit (*Myrica rubra* S. and Z.). SHIGERU KOMATSU AND RYUZAABURO NODSU. *Ibid.* 223-9(1925).—Myricitrin was isolated from the bark of Yamamomo tree. The red pigment of the fruit is composed mainly of a monoglucoside with a small quantity of the diglucoside of anthocyanidin and some free pigment. The sugar of the glucoside is *d* glucose. The sugars of the fruit are *d*-glucoses and *d* fructose in the ratio of 1.123. The non-volatile acids of the fruit are principally citric with small quantities of malic, oxalic and inactive lactic acids. H. R. K.

Conditions influencing the production of coloring matter of *Monascus purpureus* Went. SHINICHI HIRANO. *Proc. Acad. Sci. Amsterdam* 28, 182-90(1925).—Mg in low concn. (0.00001 *N*) acts as a stimulant in the production of the coloring matter. With maltose and galactose color production was extensive while with levulose it was low. O is necessary for the production of the coloring matter. The optimum temp was 27-30°. When color formation was high spore formation was high. H. R. K.

Specificity of the toxic-antitoxic combination. Utilization in plant therapy. C. PICADO. *Ann. inst. Pasteur* 39, 462-75(1925).—The addn of 0.5% NaCl and 0.21-0.6%  $\text{Ca}(\text{OH})_2$  to culture medium constitutes a toxic-antitoxic mixture which is harmless to bean plants, but which diminishes the nodosities in number and size. The complex 0.02%  $\text{HgCl}_2$  plus 0.008% S is not harmful to the plant but prevents the formation of nodosities. It is thus possible to neutralize a poison perfectly as far as the plant host is concerned, without destroying its action on an infecting parasite. E. R. L.

## E—NUTRITION

PHILIP B. HAWK

Fat digestion, absorption, and assimilation in man and animals as determined by the dark-field microscope, and a fat-soluble dye. S. H. GAGE AND P. A. FISH. *Am. J. Anat.* 34, 1-85(1924).—Fats and fatty acids were stained with sudan III or scarlet red, mixed with carbohydrate, and in many cases protein, and fed healthy men and animals.

A drop of blood was taken at every hr. during the digestive cycle and the chylomicrons ( $1$  to  $5 \mu$ ) were counted in the dark-field. Neither protein nor carbohydrates nor any combination of them gave rise to these fine particles in the blood, which are solely derived from fat of the food. These were confirmed as fat by their sepn. as a cream (2 weeks), their extn. with  $\text{Et}_2\text{O}$ , the residue staining with osmic acid, and having the  $I$  value, the refractive index and dispersion of fat. The increase of chylomicrons appears in blood in from  $0.5$  to  $1.5$  hrs. after ingestion of fat, and disappears in from  $6$  to  $10$  hrs. according to the kind and amt. of fat fed. The dyes used are absorbed into the body only when attached to a fatty acid radical. The pink fat begins to be laid down in adipose tissue in  $2.5$  hrs. after ingestion in rats, and in rats, cats and dogs it first appears in the perineal fat and in the omentum and mesentery and last in the popliteal, orbital and epidural fat masses. In all animals studied the fat was absorbed near the middle of the small intestine (and in the cat perhaps also the lower part of the duodenum, the cecum, and part of the colon). Severe mental strain in man delays fat absorption, and apparently strenuous phys. activity also retards digestion. Ingestion of castor oil or mineral oil led to no increase of chylomicrons (no absorption), but did not prevent absorption of fat ingested simultaneously. Fatty acids required much longer time for absorption than neutral fats. During fasting increase of particles only took place during and following very vigorous exercise, indicating mobilization of fat only as needed except in marked emergency. With carnivorous and omnivorous animals (cat, rat) in which fat takes a relatively important place in the natural diet the milk fat is derived largely from food fat. This does not seem to be true for the cow. The method permits also study of the development of the hen egg, indicating  $7$  or  $8$  days for complete development. The fat of the egg is largely derived from food fat. It is suggested that in diseased conditions the method demonstrates with certainty whether fatty food is digested, absorbed, and assimilated, and that it will at once indicate a pathol. hyperemia as in diabetes.

A. T. CAMERON

The influence of food on the metabolism of the leech. K. BIALASZEWICZ *Arch. intern. physiol.* 23, 218-34(1924); *Physiol. Abstracts* 9, 504(1924-5).—The respiratory metabolism of the leech is increased after eating blood proportionally to the amt. of the blood eaten without a change of the respiratory quotient. The  $N$  elimination is increased.

H. J. DEUEL, JR.

The synthesis of vitamin B by microorganisms. J. HOER G. LECLEF AND G. DELARUE. *Arch. intern. physiol.* 23, 284-98(1924); *Physiol. Abstracts* 9, 585(1924-5).—When cultures of *Monilia candida*, *Torula rosea* and *Mycoderma cerevisiae* are grown in inorg. salts and sucrose, only *Monilia* is able to synthesize vitamin B as judged by its curative action on polyneuritic pigeons and its growth-promoting property on rats fed on a diet free from vitamin B.

H. J. DEUEL, JR.

Some aspects of the mineral metabolism of farm animals. WM. GODDARD AND ALFRED D. HUSBAND. *Chemistry & Industry* 44, 671-5(1925).—Emphasis is placed on the necessity of mineral constituents in the diets of farm animals. On a diet contg.  $\text{CaCO}_3$  but deficient in Cl, a pig showed a decreasing positive Ca balance, which was not improved on the addn. of cod-liver oil; when a sufficient quantity of Cl was added, the loss of appetite and other symptoms which had ensued disappeared and an increasing positive Ca balance resulted. With the absence of Ca alone, a decreased appetite was noted with pigs and markedly subnormal growth. A deficiency of Fe in the diet of pregnant sows resulted in the death of the pigs in 3-4 weeks. On the addn. of  $\text{Fe}_2\text{O}_3$  to the diet this condition could be entirely prevented. The wt. of animals on the latter diet was three times that of animals of the same age on the Fe-free diet.

H. J. D., JR.

Vitamins. III. The vitamin content of beers. ARTHUR SCHEUNERT AND MARTIN SCHERBLICH. *Chem. Zelle u. Gewebe* 12, 45-56(1924).—The vitamin A content of the sirups of Pilsner (bottom-fermented) and Porter (top-fermented) beers which were prepd. by evaporating under a vacuum at  $42^\circ$ , was found to be inappreciable as detd. by expts. on rats. Vitamin B was present only in traces in the bottom-fermented beer while a greater quantity was found in the top-fermented beer as judged by growth-promoting power; however, in the latter on a quantity of the sirup equiv. to  $5$  l. of beer for a  $60$ -kg. rat, growth was not normal. A detectable antineuritic power was found in the bottom-fermented beer, while no vitamin C could be demonstrated in either kind of beer.

H. J. DEUEL, JR.

Vitamins. IV. The presence of vitamins A and B in horse flesh. A. SCHEUNERT AND C. HERMERSDÖRFER. *Biochem. Z.* 156, 58-62(1925); cf. preceding abstract.—Lean cooked horse flesh contg. large quantities of vitamin A failed to maintain growth of young rats on a diet free from vitamin B. Hence, horse flesh contains inadequate quantities of vitamin B.

F. A. CAJORI

Differential characters between vitamins of foods and isolated vitamins. G. LORENZINI *Arch farm sper* 39, 192-201(1925)—See C A 19, 2069 A. W. DOX

Scurvy and the antiscorbutic value of orange and lemon juice. DOMENICO LIOTTA *Arch farm sper* 39, 202-24(1925)—Orange or lemon juice contg 0.5% C1 and kept 2 months in ordinary receptacles at room temp is not attacked by molds and does not undergo fermentation. In daily doses of 5-6 cc this juice is not toxic to guinea pigs maintained on an ordinary diet. It is not a preventive of scurvy but it doubles the time required for the death of the animals from this cause. Lemon juice concd, *in vacuo* at a low temp., whether contg C1 or not, does not cure advanced scurvy in guinea pigs when given in daily doses of 6 cc but it prolongs the life of the animals about 2 weeks.

A. W. DOX

The identity of vitamin A. The comparative effects of human and cow milk. H. PRINGLE *Sci Proc Roy Dublin Soc* 18, 93-7(1925)—When a rapidly growing animal is deprived of its growth vitamin or when its supply is reduced below a critical value, its wt becomes stationary for a variable period and then suffers a marked decline. The duration of this stationary period is dependent on the supply of vitamin stored in the tissues, which in turn is detd chiefly by the quantity of fat present in the animal. The substitution of human milk in the diet of rats free from vitamin A, except for a sufficient quantity of cow milk, for the latter, resulted in a sharp drop in wt, without any previous stationary period. This suggests that human milk contains a growth retarding factor for the tissues of a more rapidly growing animal than man, or else vitamin A is one of a class of catalysts which accelerates growth according to the requirements of the particular species.

W. F. GOEBEL

The influence of a vitamin-deficient diet on the growth of mouse and rat carcinoma. LUDWIG *Klin Wochschr* 4, 1471(1925)—Cancer tissue does not develop in animals that are fed on a vitamin deficient diet prior to the implantation of the cancer tissue.

MILTON HANKE

Scurvy in a child of six and one-third years from an extraordinary dietary regime. D. J. M. MILLER *Arch Pediatrics* 42, 336-8(1925)—The diet consisted exclusively of pasteurized milk and carbohydrates, and was markedly deficient in vitamins.

JOSEPH S. HEBURN

Role of the diet in the treatment of disorders of older infants and children. F. W. SCHULTZ *Arch Pediatrics* 42, 347-62(1925)—A concise summary. J. S. H.

Lactic acid milk in the feeding of premature children. MORRIS GLEICH *Arch Pediatrics* 42, 432-9(1925)—Lactic acid milk furnishes an excellent substitute for breast milk in feeding premature babies, since the lactic acid enables the premature child to tolerate a liberal supply of fat.

JOSEPH S. HEBURN

Relationship of hard water to health. II. Effect of hard water on growth, appearance and general well-being. J. T. MYERS *J Infectious Diseases* 37, 13-31(1925)—By comparing the effect of distd  $H_2O$  and natural hard  $H_2O$  on the wt. curves of exptl animals and on the development of bone in these animals it is concluded that distd.  $H_2O$  in no case caused better development than hard  $H_2O$ , but that the reverse was true in several instances.

JULIAN H. LEWIS

Sulfur metabolism. H. B. LEWIS *Physiol Rev* 4, 394-423(1925)—Review with extensive bibliography.

E. R. LONG

The nutritive value of the proteins. H. H. MITCHELL *Physiol Rev* 4, 424-78(1925)—Review with extensive bibliography.

E. R. LONG

Analysis of vitamin-containing foods. (MRS.) L. RANDOIN *Ann fals.* 18, 325-31(1925)—Brief outline of the position of vitamins in a complete diet, and of the method of detg them in prep'd foods to verify the claims put forth by the mfrs.

A. P.-C.

Basal metabolism in cases of underfeeding. MARCEL LABBÉ AND HENRI STÉVENIN *Presse médicale* No 25, 401(1925); *Bull soc. hyg aliment* 13, 306(1925)—Continuous underfeeding results in a basal metabolism 11-39% below normal, and detn. of basal metabolism can be of very great value in diagnosing such cases and differentiating from Basedow's disease or from tuberculosis.

A. PAPINEAU-COUTURE

The influence of aliphatic ethers on the elimination of nitrogen. U. G. BILSMA *Arch néerland physiol* 9, 276-7(1924)—Dogs were given 100-300 mg. of ethyl acetate or amyl valerate daily for 4-6 days. The urine nitrogen was increased 11.5% and the fecal nitrogen was also augmented. The increase was due to a toxic action on the body proteins as well as an increase in metabolism.

M. H. SOULE

Relation of the vitamins to the reactions induced by coal tar in the tissues of animals. L. H. JORSTAD *J Exptl Med* 42, 221-30(1925)—Drops of coal tar introduced into the subcutaneous tissue attract the fibroblasts, endothelial and other cells to them. These cells suffer degenerative changes through this action of the tar and the

animal suffers cachectic-like changes and death from large doses of it introduced into the subcutaneous tissue. This action of the coal tar is limited to a short period of time, after which it becomes inert. The cells which have been drawn to it and which have not completely degenerated then slowly recover. Vitamin A fed in more than ample quantities to these animals protects the animals and the cells against the toxic action of the tar and stimulates and prolongs their secondary growth. Vitamin B stimulates the secondary growth of these cells. This action is limited in extent and time. It is followed by an early degeneration and hyalination of the tissue. C. J. WEST

## F—PHYSIOLOGY

ANDREW HUNTER

The hormone of the ovarian follicle; its localization and action in test animals and additional points bearing upon the internal secretion of the ovary. E. ALLEN, B. F. FRANCIS, L. L. ROBERTSON, C. E. COLGATE, C. G. JOHNSTON, E. A. DOISY, W. B. KOUNTZ and H. V. GIBSON. *Am J Anat* 34, 133-82(1924).—The seat of production of the principal ovarian internal secretion is localized in the follicle, as demonstrated by successful substitution of injections of liquor folliculi and exts. of follicular contents for the endocrine function of normal ovaries, at least in absence of pregnancy. Several injections of the active substance into spayed rats and mice induce the accelerated growth, hyperemia, and secretion in the genital tract characteristic of estrus, and equal in degree to the max. in the normal animal under ovarian influence. Such spayed rats behave normally sexually, indicating that sex instincts are ultimately dependent on this internal secretion. After the injected material is exhausted degeneration sets in in the changed tissue, so that alternate presence and absence of this secretion is sufficient to supply the causative mechanism of the estrous cycle. Injections into immature animals cause premature attainment of maturity. The artificial estrus test used can be employed to standardize exts. The production of the secretion seems referable ultimately to the metabolism of the ovum itself. The corpus luteum is a gel in contrast to the fluid state of the liquor folliculi. No growth-producing ext. has been obtained from corpus luteum of either estrus or pregnancy. A. T. CAMERON

The influence of natural chemical stimuli on the movements of the alimentary canal. B. P. BABKIN. *Can. Med Assoc J* 15, 719-21(1925).—A review, dealing very largely with his own work. A. T. CAMERON

General characteristics of the activity of the nerves and muscles. J. S. BERITOFF. *Ergebnisse Physiol* 23, 1 Abt. 33-76(1924).—A review. H. J. DEUEL, JR.

The increasing importance of the permeability problem for physiology and pathology. H. J. HAMBURGER. *Ergebnisse Physiol* 23, 1 Abt. 77-98(1924).—A discussion on the mechanism of absorption. The permeability of the salivary glands and the mucosa of the intestines is discussed in this connection as well as the physical chemical mechanism in nerve activity. II. emphasizes that the permeability of different cells is not the same nor does that of a single cell remain constant but depends largely on external conditions. II. Vital permeability. *Ibid* 99-119.—The permeability of the cells varies with differences in the composition of the surrounding media. When the kidney of the frog is perfused with ordinary Ringer's soln. glucosuria was obtained. However, when the  $\text{CaCl}_2$  and  $\text{NaHCO}_3$  is increased ( $\text{NaCl}$  0.5,  $\text{KCl}$  0.01,  $\text{NaHCO}_3$  0.285 and  $\text{CaCl}_2$  0.015%) subsequent perfusion did not cause glucosuria. The  $\text{Ca}$  ion in some way regulates permeability while the  $\text{NaHCO}_3$  concn. detrs. the amount of  $\text{Ca}^{++}$  present. The  $\text{Ca}$  which is available in un-ionized form has no effect on the permeability. These phenomena are of importance in explaining the impermeability of the glucose into the blood corpuscles. III. Vital permeability. *Ibid* 120-38.—This section deals with the causes of impermeability of the kidney for glucose. This condition cannot be due to the size of the molecule, since disaccharides are excreted, but must in some way be related to the stereoisomerism. In diabetes, it is suggested that glucose may be transformed into an isomeric form which can be excreted. H. J. DEUEL, JR.

The present status of the physiology of the parathyroids. C. JACOBSON. *Ergebnisse Physiol* 23, 1 Abt. 180-211(1924).—A review. H. J. DEUEL, JR.

The effect of total extirpation of the liver. F. C. MANN and T. B. MAGATH. *Ergebnisse Physiol* 23, 1 Abt. 212-73(1924).—A review. A method for the total extirpation of the liver is described by which animals can be kept alive for many hrs. after the operation if glucose is administered. The conclusions are drawn that the liver is absolutely essential for the regulation of the blood-sugar level, that this organ is the most important if not the only site in the deamination and urea synthesis, and that bilirubin can be formed without the liver. H. J. DEUEL, JR.

The behavior of the gastric and intestinal secretion after the removal of the gall bladder. FRANZ ROST *Mitt Grenz Med Chir.* 38, 1-7(1924).—The removal of the gall bladder in dogs with gastric and intestinal fistulas did not cause any change in the reaction of the gastric juice of the mixt. of bile and pancreatic juices; the enzyme content likewise remained unaltered. H. J. DEUEL, JR.

The oxidation of acetic acid, acetone and toluene. F. KNOOP AND M. GEHRKE, *Z. physiol. Chem.* 146, 63-71(1925).—If AcOH, which is so readily formed *in vitro* by oxidation of aliphatic substances, could be shown to undergo by further oxidation a condensation to succinic acid this would afford a possible explanation of the biol. occurrence of tartaric, malic, aspartic and pyruvic acids. However, AcOH is very resistant to oxidation and the succinic acid that might be formed would be less stable and therefore difficult to demonstrate. After AcOH was subjected to the action of  $H_2O_2$  for several weeks in the thermostat, 96-98% was recovered. Only a trace of non-volatile substance was obtained, it was not sufficient in amt. for identification but it showed certain properties of tartaric acid. MeAc is more readily attacked, and from 15 g. 60% was recovered, while 498 mg. tartaric, 21 mg. malic and 6 mg. succinic acid were obtained. The oxidative synthesis of a 4-carbon chain is thus demonstrated. The oxidation of PhMe to BzOH might by analogy be expected to occur through a similar condensation with intermediate formation of  $(PhCH_2)_2$ . After oral administration of 7g. PhMe to a dog a 76% yield of hippuric acid was obtained in the urine, while  $(PhCH_2)_2$  gave no increase over the normal hippuric acid excretion but was eliminated for the most part unchanged. The Et<sub>2</sub>O ext. of the urine showed in this case a small amt. of stilbene, thus an apparent dehydrogenation. Evidence was obtained that the stilbene resulted from hydrolysis and dehydration of the corresponding alc., which was present as a glucuronate. On the other hand, the fact that feeding of the alc. and ketone  $(PhCH_2)_2$  does not increase the normal excretion of free or conjugated BzOH shows that neither of these substances can be regarded as an intermediate product in the oxidation of PhMe to BzOH. A. W. DOX

The effect of ultra-violet irradiation on the state of the serum calcium. A. R. MORITZ *J. Biol. Chem.* 64, 81-9(1925).—Place 2 cc. of serum in a sac made from a soln. of 10 g. Parlodion and 5 cc. olive oil in 50 cc. abs. EtOH and 50 cc. Et<sub>2</sub>O and dialyze 4 hrs. against 5 cc.  $H_2O$  in a 15-cc. centrifuge tube, maintaining a negative pressure of 150 mm. Hg on the dialyate. Det. the Ca in the dialyate by Kramer and Tisdall's method (*C. A.* 17, 2804). About 55% of the serum Ca dialyzes in 4 hrs. and there is no increase on further dialysis. Serum kept 48 hrs. in the refrigerator gives about the same value (av. 58%) but serum kept 48 hrs. at room temp. gives an av. of 72%. "No changes in the total Ca nor in the % of diffusible Ca of the blood serum of normal rabbits were observed following ultra-violet irradiation *in vitro* or *in vivo*." I. O.

Investigation on the crystalline lens. DOROTHY R. ADAMS *Proc. Roy. Soc. (London)* 98B, 244-50(1925).—Use was made of crystalline lenses of the ox and the sheep. The lens has a definite O intake, which is increased in the presence of glutathione and, to a greater extent, in the presence of both glutathione and linseed oil. The power to use O is impaired by drying the lens and is lost on its dialysis, but is fully restored on addition of a few mg. of glutathione to the suspension of dried or dialyzed lens. A thermostable residue may be prepd. from the lens; this residue has no O uptake of its own, but gives typical O uptake curves with glutathione and with that compd. plus linseed oil. Of the 3 proteins in the lens, only  $\beta$  crystallin can function as a thermostable residue. The lens is able to oxidize certain org. acids (fumaric, malic, succinic), but this power is decreased by exposure to ultra-violet light. The glutathione content of the ox lens (av. value 0.305%) is decreased by exposure to ultra-violet light, and, to a more marked extent, by exposure to heat rays. JOSEPH S. HEPBURN

Muscular exercise, lactic acid, and the supply and utilization of oxygen. X. The oxygen intake during exercise while breathing mixtures rich in oxygen. K. FURUSAWA, *Proc. Roy. Soc. (London)* 98B, 287-9(1925); cf. *C. A.* 19, 2368.—The max.  $O_2$ -intake may be increased 50% by breathing a mixt. rich in  $O_2$ , as a result of an increased circulation rate of the blood. JOSEPH S. HEPBURN

The regulation of the sugar of the blood and the reaction of the blood in men. III. The regulation of the sugar of the blood in changes of reaction of the blood. G. ENDRES AND H. LUCKE, *Z. ges. exp. Med.* 45, 669-81(1925); cf. *C. A.* 19, 2521.—The alkalosis caused by hyperventilation of the lung is accompanied by hypoglycemia which in about half the cases is followed by a slight hyperglycemia. In natural sleep the sugar content of the blood is increased up to 25% and this is perhaps related to the increased H<sup>+</sup> content of blood in sleep. The regulation of the amount of sugar in the blood seems more influenced by changes in the reaction of the blood than is the mechan-

ism for regulation of the reaction of the blood by changes in the sugar content of the blood

HARRIET F. HOLMES

The synergic effect of the endocrine glands on bone formation. MATTEO MANELLI *Gazz Internat Medico-Chirurgica* 4(1925), *Rass clin terap sci affini* 24, 138-56(1925) — Thyroidectomy or injections of fecal matter gave rise to rachitiform alterations in the ossification process of bone fractures Treatment with combined thyroid, pituitary, ovarian and testicular exts arrested the pathological process and ensured a more normal ossification

MARY JACOBSEN

The extrahepatic formation of bile pigment. A R RICH *Bull Johns Hopkins Hosp* 36, 233-47(1925) — "Bile pigment may continue to be formed to the point of tissue jaundice in dogs from which the liver and all other abdominal viscera have been removed if an active circulation be maintained throughout the entire musculo-skeletal system The amt of bile pigment formed after hepatectomy may be increased by the intravenous injection of hemoglobin There exists an as yet unidentified extrahepatic mechanism which, if it is not continually active under normal conditions, is undoubtedly able to form bile pigment on immediate notice in the absence of the liver In contrast with the failure of bile pigment to appear in the plasma or tissues in expts in which the circulation was restricted to the head and thorax, the pigment may appear in a time much shorter than the duration of these expts if the arterial blood supply to the liver be added to the 'head-thorax circulation' after obstruction of the common and cystic ducts We are unable to speak at present with any certainty about the mechanism by which bile pigment is formed in an hepatectomized animal, and the normal site of origin of bile pigment still remains a problem"

A P LOTHROP

Placental transmission. III. The amino acids, non-protein nitrogen, urea, and uric acid in fetal and maternal whole blood, plasma and corpuscles. E. D. PLASS AND C. W. MATTHEW *Bull. Johns Hopkins Hosp* 36, 393-402(1925), cf *C A.* 17, 2734 — "The amino acids and total non-protein N are uniformly higher in normal fetal whole blood and plasma than in the maternal Urea is usually found in equal concns. in the 2 bloods. Uric acid is usually found in equal concns in the 2 circulations but, if there is a difference, it is generally higher in the fetal blood" The fetus is thus assured of an abundance of the essential "building stones" and it is evident that the amino acids do not pass the placenta by simple diffusion

A P LOTHROP

The bile-pigment content of the splenic vein. A R RICH AND WM F. RIENHOFF, JR. *Bull. Johns Hopkins Hosp.* 36, 431-6(1925).—In 4 out of 10 cases blood from the splenic vein contained much more bilirubin than control blood from the splenic artery and peripheral veins, evidence that bilirubin can be formed in the spleen In pernicious and secondary anemias this may or may not be the case In a case of hemolytic jaundice the bilirubin content of the splenic vein was high but following splenectomy it fell to normal within 48 hrs.

A P LOTHROP

The distribution of glucose between human blood plasma and red corpuscles and the rapidity of its penetration. R EGE, E GOTTLEB AND N. W. RAKESTRAW. *Am. J. Physiol.* 72, 76-82(1925).—In normal human beings the distribution of glucose between corpuscles and plasma lies between 74.100 and 95.100 Conditions of collecting the blood for analysis have little effect on this ratio. Glucose added to blood at body temp. is distributed almost immediately between plasma and corpuscles. When corpuscles are suspended in pure glucose soln the rate of penetration is much slower. Temp. has a great influence on the rate of penetration; at 40° penetration is 10 times as rapid as at 30°.

J. F. LYMAN

The dissociation of oxyhemoglobin in the tissues. J. A. CAMPBELL. *J Physiol* 59, 395-406(1925).—Gas injected under the skin of an animal and allowed to remain until equil. is established undergoes changes as a result of muscular exercise Changes in CO<sub>2</sub> content parallel the changes in the alveolar air. The O<sub>2</sub> tension is increased by muscular exercise by about 25%, probably due to the action of lactic acid upon the dissociation of oxyhemoglobin Insulin injections have the same effect as muscular work. Conditions that produce tetany, forced artificial respiration, NaHCO<sub>3</sub> injection of guanidine, greatly reduce O<sub>2</sub> tension in the gas under the skin. This fall may be due, in part, to alkalosis.

J. F. LYMAN

The influence of chemical factors on the coronary circulation. R. HILTON AND F. EICHMOLTZ *J. Physiol* 59, 413-25(1925).—Changes in O<sub>2</sub> tension of the blood flowing through the coronary vessels, rather than the presence of metabolites, are responsible for the state of dilatation of the vessels and the regulation of the rate of flow.

J. F. LYMAN

Pancreatic secretion. G. V. ANREP, JOAN L. LUSH AND M. GRACE PALMER. *J. Physiol* 59, 434-42(1925) —The concns. of all three enzymes of the pancreatic juice

show a parallel fall when the gland is stimulated at a constant rate by secretion for a long time. A new method for lipase estn. is described. J. F. LYMAN

The influence of the vagus on the islets of Langerhans. I. Vagus hypoglycemia. C. A. CLARK *J. Physiol.* 59, 466-71 (1925).—Drugs that stimulate the parasympathetic system were shown to cause a lowering of blood sugar in the rabbit. This effect was not produced in most cases after cutting the right vagus. It is suggested that stimulation of the vagus causes a secretion of insulin. J. F. LYMAN

Physiological properties of substances elaborated in the isolated thyroid. G. A. MALOFF *Arch. ges. Physiol.* (Pflüger's) 208, 335-42 (1925).—The vessels of the isolated thyroid of the dog react readily and promptly to vasoconstricting agents (adrenaline, nicotine,  $\text{BaCl}_2$ ) and to vasodilating substances (caffeine, especially, and quinine). The perfusion fluid (Ringer Locke) which has passed through the vessels of the isolated thyroid contains substances which increase the irritability of the sympathetic nerve endings and which render the vessels of the isolated liver susceptible to adrenaline. These substances also cause a vasoconstriction of the vessels of the isolated rabbit ear. Apparently they are elaborated by the gland since their presence can be demonstrated in both the first and the last portions of the perfusion fluid to pass through. The substances thrown into the perfusion fluid are without action upon the isolated heart, the vessels of the isolated extremities, and the liver of the frog. G. H. S.

General cellular physiology. III. Osmotic and colloid properties of striated and smooth musculature. ERNST GELLHORN *Arch. ges. Physiol.* (Pflüger's) 208, 379-92 (1925), cf. *C. A.* 18, 858.—Preliminary treatment with hypertonic NaCl solns diminishes the shrinking in isotonic  $\text{CaCl}_2$  and increases the swelling in isotonic KCl or in NaCl contg. 0.01 N HCl. Previous treatment with hypotonic solns has the opposite effect upon the changes taking place in  $\text{CaCl}_2$ , KCl or HCl. These effects are due to the combined action of osmotic and imbibition processes. If two muscles are given a preliminary treatment with isotonic  $\text{CaCl}_2$  or KCl, and thereby attain very different states of swelling, their increase in wt. when brought into a hypotonic NaCl soln is the same. Only after a very long preliminary treatment can it be shown that the increase in wt. taking place in 0.3% NaCl is greater after exposure to KCl than after  $\text{CaCl}_2$ . But muscles which have reached a different degree of swelling through exposure to  $\text{CaCl}_2$  or to KCl react very differently to hypotonic solns, in that the tissue treated with KCl loses in wt. much more than does the muscle treated with  $\text{CaCl}_2$ ; and this difference is the greater as the soln. is the more hypotonic. In these respects striated and smooth muscles exhibit no material differences. The state of the muscle colloids, the globulin in particular, is so changed by the action of concd. solns. of NaCl,  $\text{MgSO}_4$ , and  $(\text{NH}_4)_2\text{SO}_4$  that the normal swelling in KCl or shrinking in  $\text{CaCl}_2$  does not take place. Either the swelling occurring in both solns. is the same or the effects are reversed. By detg. the max. concn. of NaCl or  $\text{MgSO}_4$  to which the tissues can be exposed and still retain their normal reactions to KCl and  $\text{CaCl}_2$ , it is found that the salt susceptibility of smooth muscle is materially greater than that of striated muscle, the colloids of the smooth muscle appear thus to be relatively hydrophobic. G. H. S.

Results of extirpation of the thyroid. ERN. ABBERHALDEN, *Arch. ges. Physiol.* (Pflüger's) 208, 476-86 (1925).—After extirpation of the thyroid the results exhibited by different individuals may be extremely divergent; profound disturbances occur in some, minor disturbances in others. Also, in some individuals the recovery from the effects of thyroid removal are practically complete, in others there is but little tendency to regain normal function. In many instances where the normal conditions seem to be restored the recovery is apparent only. In any case, an animal deprived of its thyroid tissue is never the same as a normal animal. G. H. S.

Delivery of nitrogen by isolated frog muscles due to the action of substances causing chemical contraction. ORRO RIESSER, *Arch. ges. Physiol.* (Pflüger's) 208, 522-8 (1925).—Fresh, isolated frog gastrocnemii yield, in Ringer soln. under an abundant O supply, on an av. 0.0175% of their wt. of N within a period of 3 hrs. The N elimination later falls to 0.006 to 0.005%. N elimination is not modified by fatigue, KCl contraction, isotonic cane sugar, or narcotics with 4 to 10% alc. It is, however, very considerably increased by HCl, NaOH,  $\text{CHCl}_3$ , and bromoacetic acid when these substances are used in concns. which induce contraction. This increased N delivery must be viewed as an expression of a more or less profound injury to the muscle, as is particularly obvious after treatment with  $\text{CHCl}_3$ . G. H. S.

Formation of urine in the frog kidney. VI. Effect of temperature upon the function of the surviving frog kidney. ERICH DAVID, *Arch. ges. Physiol.* (Pflüger's) 208, 529-34 (1925).—Temp., through the range 0-30°, has no direct influence upon the capacity of the surviving frog kidney to effect diln. or concn. Temp. modifies only the

degree of dilatation of the kidney vessels, and in this way indirectly affects the concn. of the urine. G. H. S.

Experimental study of the relation of the ovary to fat metabolism. M. T. BULLOWS AND C. G. JOHNSTON. *J. Exptl. Med.* 42, 215-9 (1925).—The follicular fluid of the ovary contains an active growth-stimulating substance, capable of initiating an active digestion of a foreign fat, which might otherwise remain unabsorbed for an indefinite period of time in the tissues. C. J. WEST

Liberation of adsorbed substances from proteins. A function of the bile salts. I. Preliminary report. S. M. ROSENTHAL. *J. Pharmacol.* 25, 449-57 (1923).—Ultrafiltration studies have shown that rose bengal and bromosulfonphthalein, dyestuffs that are excreted in the bile, and bilirubin are *in vitro* completely bound to the proteins of the blood. Na taurocholate exerts a marked activity in the liberation of these substances from the proteins. Phenolsulfonephthalein circulates in the blood partly bound to the proteins. Bile salts are also capable of freeing the bound portion of this dye, so that *in vitro* it becomes almost entirely diffusible. Na taurocholate possesses the property of increasing the degree of permeability of semipermeable colloidal membranes to dyestuffs. These properties of the bile salts indicate their physiol. function in the liberation from a bound state of substances that are combined with the body proteins and suggest a further influence upon membrane permeability. C. J. WEST

The variations of the electrical resistance of the muscles caused by various physical and chemical agents. FIL. BORTAZZI AND L. DE CARO. *Atti accad. Lincei* [6], 1, 573-8, 635-8 (1925).—B and C have detd. the elec. resistance of muscle long immersed in solns. having various pH values. Connective membranes (omentum, pericardium, tendinous center of the diaphragm) have a smaller elec. resistance than the muscular part of the diaphragm. The course of the elec. resistance of surviving diaphragm at const. temp. (24.5°) is peculiar, it first diminishes a little, then increases considerably and finally shows a progressive strong diminution. The 1st 2 parts of the curve are hard to interpret. The last phase represents a progressive increase in permeability due to mortal changes. It is singular that both in contraction in the cold and in the hot and more so in rigidity in the cold and in the hot there is a corresponding diminution in the elec. resistance. Probably in these cases this is the expression of an increase of the permeability of the muscle fiber for the ions. The elec. resistance of the muscle shows a minimum value at pH 4.6-5.1, which corresponds to the minimum of imbibition of muscles found by Quagliariello (*C. A.* 19, 1590). R. J. WITZMANN

The parotid secretion of man excited by various peripheral factors. V. DE LAURENZA. *Atti accad. Lincei* [6], 1, 599-601 (1925).—Brunacci (*C. A.* 5, 3085, *Arch. fsiol.* 12 (1914); 13 (1915), 15 (1917), *C. A.* 7, 2802) made a series of studies on the variations of the physical chem. properties of saliva with chem., gustative, olfactory and psychic excitement, etc. L. has undertaken this study using the same method. The previous knowledge of the action of HCl, NaCl, sucrose and quinine on the gustative terminations to excite the rhythm of the parotid secretion was confirmed. Glycerol, ext. of *Capricum annum longum* and stovaine act to a different degree and presumably by a different mechanism. 95% EtOH, MeOH, PrOH and iso BuOH show different actions in 2 subjects: in 1 case it inhibits and in the other it promotes secretion in the same conditions. Heat and cold applied to the oral mucosa show no appreciable action. The stimulus of pain on the tongue (needle) gave positive results. The movements of deglutition, of mastication and of opening and closing the mouth stimulate secretions. The secretion is diminished during muscular labor. After a 10% soln. of stovaine had acted locally 10-15 mins. the ext. of "capsicum" and 1% HCl showed their normal effects on the secretion. The threshold limits of excitement were for HCl 0.015%, for  $C_{12}O_2H_2$  0.0066 N, for sucrose 2%, for quinine 0.01-0.02%, for NaCl 0.43%. With successive and gradual increase in the intensity of stimulation in these cases the secretory effect is not increased proportionally. R. J. WITZMANN

The rhythm of parotid secretion in man and gustative and olfactory sensations. NAZZARENO GRISOGANI. *Atti accad. Lincei* [6], 1, 602-4 (1925).—The parotid secretion in man under the continuous and uniform action of gustative and olfactory agents constantly shows periodic oscillations in which phases of secretion alternate with phases of complete suspension of salivary flow. Under the influence of gustatory influences the flow is more abundant; the crests of the rhythmical waves are higher. The amt. of this elevation varies with the gustatory agent used; it is greatest for bitter and sour, less for sweet and more prolonged for salty agents. Similar variations are obtained when the lingual nerve endings are effaced with a  $Me_2CO$  ext. of "capsicum". The odor of AcOH vapors has an evanescent effect; while  $NH_3$  vapors show no effect. The essence of mint, cloves, lavender and rosemary show a variable stimulating action on the se-

cretion  $\text{CH}_3$ ,  $\text{C}_2$ ,  $\text{PhMe}$  and capryl alc. show a depressing action. The effects vary with the subject and are positive or negative, depending upon whether they are pleasing or displeasing. When mixed odors having a positive and negative effect on a given subject are used the effect of the latter prevails. E. J. WITZEMANN

## G—PATHOLOGY

H. GIBSON WELLS

Cystinuria. A. MAGNUS LEVY. *Biochem. Z.* 156, 150-60 (1925).—The metabolism of a patient excreting cystine was followed. Larger quantities of cystine were excreted on protein high diets and during periods when the patient had a fever due to infection. The highest daily excretion during fever was 1.6 to 1.8 g. of cystine. F. A. C.

Blood in personality disorders. Biochemical studies. G. W. HENRY AND ELIZABETH MANGAM. *Arch. Neurol. Psychiatry* 13, 747-9 (1925).—Data of the  $\text{CO}_2$ -combining power of 200 patients consecutively admitted to a hospital indicate that this is unaffected by psychoses unless there is some definite accompanying physical disease. Results (with fewer patients) for blood urea N, non-protein N, uric acid, glucose, and Cl were negative. Glucose tolerance tests indicated a definite retardation of function of the vegetative nervous system (decreased tolerance) in manic depressive depression and in the acute stage of dementia praecox, and an acceleration (increased tolerance) in manic depressive excitement. A. T. CAMERON

The cerebrospinal fluid in tumor of the brain. R. G. SPURLING AND C. L. MADDOCK. *Arch. Neurol. Psychiatry* 14, 54-63 (1925).—The normal ventricular fluid only differs markedly from the normal spinal fluid by its protein content, 3 or 4 times greater. Spinal fluid in brain tumor shows low cell count, high total protein, a characteristic *Au curve*, and no significant glucose variations. The ventricular fluid shows similar changes. In chronic arachnoiditis both fluids are normal. A. T. CAMERON

A study of the lipoids in neuronie degeneration and in amaurotic family idiocy. G. W. HURST. *Brain* 48, 1-42 (1925).—A histochem. study, from which it is concluded that the phosphatides and cerebroside found in these conditions have been liberated from chem. combination with some other radicals, probably from lipoproteins. A. T. CAMERON

Diagnosis and prognosis in chronic renal disease: the range of urea concentration or range of function test. E. G. B. CALVERT. *Brit. Med. J.* 1925, 1, 84-7.—In estg. kidney function note should be taken not only of the degree to which concn. of waste products can occur, but also of the capacity of the kidneys to produce a dil. urine. Power to conc. urea is best detd. during the night; value of the results is enhanced by detn. of greatest extent to which  $\text{H}_2\text{O}$  diuresis, most effective during waking hrs., can lower the concn. of the urea. A. T. CAMERON

Blood calcium and inorganic phosphates in children with marked lack of muscle tone. LUCY WILLS. *Brit. Med. J.* 1925, 1, 302-4.—Normal Ca range and av. (10 children) was 10.1-11.0, 10.4; inflamed tonsils and adenoids but good muscle tone (20 cases) 8.7-10.6, 9.8; marked lack of muscle tone (30 cases) 6.6-10.6, 9.0 mg. per 100 cc. serum. Approx. the same normal values were found for all 3 classes for inorg. phosphates. No relationship was established between the Ca level and muscle hypotonus. The blood picture of flabby children is not similar to that of rachitic children. A. T. CAMERON

The influence of Röntgen rays on the tissue content of cholesterol. A. H. ROFFO. *Bull. soc. chim. biol.* 7, 508-14 (1925); cf. *C. A.* 19, 1286, 1736.—Irradiation of pathological tissue (chiefly carcinomas) with X-rays leads to a marked diminution of blood cholesterol, distinct after 0.5 hr., and usually progressive for 24 hrs. A. T. CAMERON

Influence of rubidium, selenite and selenate ions on the respiration of normal and neoplastic cells. A. H. ROFFO AND S. M. NEUSCHLOS. *Bull. soc. chim. biol.* 7, 515-21 (1925).—See *C. A.* 19, 2240. A. T. CAMERON

Ultrafiltrable calcium in cancerous serum. A. H. ROFFO AND L. M. CORREA. *Bull. soc. chim. biol.* 7, 522-5 (1925).—About 62% is ultrafiltrable. A. T. CAMERON

The calcium and inorganic phosphorus content of the blood serum in tuberculosis; observations on patients undergoing Alpine lams treatment. M. G. HOWE AND E. M. MEDLAR. *Am. Rev. Tuberculosis* 10, 408-30 (1921).—There is no evidence of an abnormal metabolism of Ca or P in the tuberculous patient. There is no evidence that ultra-violet rays have any effect upon the Ca or P content of the blood, granted their concn. is within normal limits before treatment. H. J. CORPER

The Daranyi flocculation reaction in pulmonary tuberculosis. MAX PINNER. *Am. Rev. Tuberculosis* 10, 411-8 (1921).—The Daranyi test (*C. A.* 17, 1664, 581) is of

little diagnostic value in tuberculosis, but appears to be a sensitive indicator of alterations in the colloidal stability of the serum in diseased conditions, and gives valuable information as to the severity of the destructive process. H. J. CORPER

Serum precipitation findings in active tuberculosis. FELIX BAUM *Am. Rev. Tuberculosis* 10, 449-53 (1924) H. J. CORPER

Tuberculosis and the serum calcium mirror. FRANZ KRÖMEKE *Beitr. klin. Tuberk.* 57, 467-75 (1924) —The irritability of the vegetative nervous system in tuberculosis results in disturbances of the Ca content of the tissues and the blood. The quantity of free Ca ions cannot be detd. accurately in the blood. In order to study the relation between the Ca metabolism and the various forms of tuberculosis, the total Ca content of the blood was detd. (method of DeWaard) on 45 tuberculous patients. Of these cases 20, including the various forms with the exception of the exudative, revealed normal serum Ca content (10.5 to 11.5 mg. %), and there were no marked disturbances of the vegetative nervous system. In 8 of the cases there were high values (11.5 to 12 mg. %). These values were found mostly in productive tuberculosis of widespread nature, while normal values were overstepped in favorable or fibroid cases. Among the 8 cases with hypercalcemia there was one patient with an acinous-nodose active process and increased irritability. Aside from this there were 3 cases with hyperirritability. Hypocalcemia was found in 9 patients, one an asthenic type with fibrotic inactive tuberculosis. Six in this group revealed hyperirritability with prominent vagotonic symptoms and 4 of these had an exudative tuberculosis of severely destructive type. One of the cases with low blood Ca was an old indurative, inactive case with calcified apical tuberculous. Besides the serum Ca detn. the globulin pptn. reaction of the serum (according to Matefy) was tested with resultant marked globulin increase in the exudative tuberculous cases. There was no direct relation between the relative globulin increase and the Ca. Likewise there was no relation between these and the grade of tuberculosis allergy. H. J. CORPER

The treatment of infantile tetany. GRACE H. ANDERSON *Glasgow Med. J.* 103, 159-63 (1925) —The use of  $\text{CaCl}_2$  is recommended in this condition. H. J. DEUEL, JR.

Tetany: the blood chemistry. STANLEY GRAHAM *Glasgow Med. J.* 103, 162-8 (1925) —A discussion of the various theories on the causation of tetany. H. J. D., JR.

The hypophysis and basal metabolism. J. M. PAREJA *Anal. facultad med.* 8, 1102-17 (1923); *Physiol. Abstracts* 9, 599 —Basal metabolism is increased in acromegaly and in gigantism, decreased in Froehle's syndrome and in diabetes insipidus. Diseases of the pituitary are frequently associated with those of other endocrine glands, which also influence the basal metabolism. H. G.

Cholesterol, albumin, and globulin in cases with a diminishing blood sedimentation rate. H. GROSSMAN *Z. ges. expil. Med.* 42, 496 (1924), *Physiol. Abstracts* 9, 575 —In 8 out of 9 cases with diminishing velocity of sedimentation of the red blood corpuscles the cholesterol percentage of the serum increased and the albumin exceeded the globulin. After addn. of cholesterol suspension the velocity continued to diminish. H. G.

The mechanism of reaction of nonspecific protein agents in the treatment of disease. II. The influence of various agents on the mobilization of blood antibodies. C. Y. LING. *Arch. Intern. Med.* 35, 740-51 (1925), cf. *C. A.* 19, 2085. —The sera of patients and rabbits contain more bacteriolysin for *B. typhosus* and *Staphylococcus aureus* and bacteriotropin for *Staphylococcus aureus* 24 hrs. after the injection of  $\text{H}_2\text{O}$ , auto-serum, horse serum, certified milk, market milk, crotalin, peptone or typhoid vaccine than before such injection. Typhoid vaccine and market milk are the most effective in increasing the amt. of bacteriolysin against *B. typhosus* and *Staphylococcus aureus*. Peptone and market milk are most effective in increasing the opsonic index against *Staphylococcus aureus*. Four hrs. after all of the injections, except horse serum and auto-serum, the antishoop hemolytic complement titer was lower than in the controls, rising again at the end of 24 hrs., but only after horse serum and auto-serum was the titer higher than in the controls. None of the substances injected had any effect upon the content of natural antishoop hemolysin. Bfeeding and the accompanying slight trauma act as a mild form of nonspecific protein agent and produce the usual response. III. The influence of various agents on the mobilization of blood enzymes in normal persons and in rabbits. *Ibid.* 752-9 —Four hrs. after the injection of  $\text{H}_2\text{O}$  or of auto-serum, the fall in the ability of the serum to digest its own proteins, after treatment with  $\text{CHCl}_3$ , was of about the same slight extent as in the controls. At the end of 24 hrs., the proteolytic activity was less than in the control with auto-serum and slightly greater with  $\text{H}_2\text{O}$ . Crotalin, certified milk, market milk, typhoid vaccine, horse serum, and peptone, in the order named, gave increasing proteolytic activity 4 hrs. after the injection, with decreases to far below the control in 24 hrs., to slightly below after horse serum and

peptone and slightly above alter the others. The ability to digest peptone, as judged by the reaction with  $\text{Br}_2$ , was decreased 4 hrs. after the injection of peptone, autoserum and typhoid vaccine, was increased after market milk, horse serum, certified milk,  $\text{H}_2\text{O}$  and left unaffected by crotalin. After 24 hrs., the activity of all sera after injections was greater than in the control. The lipolytic activity,  $\text{EtOBU}$  being used, was decreased 4 hrs. after the injection of peptone, crotalin,  $\text{H}_2\text{O}$ , autoserum and increased 4 hrs. after the others, decreased 24 hrs. after horse serum, typhoid vaccine, crotalin,  $\text{H}_2\text{O}$  and autoserum and increased after the others. I. GREENWALD

Leucemia. The relative values of cell morphology and the peroxidase reaction as diagnostic aids. M. N. RICHTER. *Arch. Intern. Med.* 36, 13-23(1925).—"The peroxidase reaction is of less value in diagnosis than the study of stained smears." I. GREENWALD

Blood volume. VI. The relationship between blood volume, total corpuscle content and alkaline reserve in cases of pernicious anemia. WINIFRED ASHBY. *Arch. Intern. Med.* 36, 24-30(1925); cf. *C. A.* 19, 2073.—In patients with pernicious anemia, the alk. reserve, as detd. from the urine by the method of Fitz and Van Slyke (*C. A.* 11, 2224) was frequently below the normal but tended to become normal after transfusion. The change is, probably, due chiefly to the increase in red cell count, although mere increase of blood vol. also tends to increase alk. reserve slightly. I. G.

Acute intestinal obstruction. III. Simple obstruction. W. C. POSTER AND R. W. HAUSLER. *Arch. Intern. Med.* 36, 31-43(1925); cf. *C. A.* 19, 331.—"Death in uncomplicated cases (dogs) of acute intestinal obstruction is due to starvation. The blood chemistry changes are almost identical with those found in complete starvation. Hypochloremia is not present. Dehydration is usually very pronounced." I. G.

Hypoglycemia. Report of a case unassociated with insulin administration. LIU SHIH HAO AND CHANG HSIAO-CHIEN. *Arch. Intern. Med.* 36, 146-8(1925).—The patient, after several days' diarrhea, followed by administration of castor oil and enemas, developed a tetany-like condition but with normal  $\text{Ca}$  (11.3 mg. per 100 cc.) and normal  $\text{CO}_2$ -capacity (50.4%) with low blood sugar (75 mg. per 100 cc.). I. G.

Hourly hemoglobin variations in anemias. E. S. MILLS. *Arch. Intern. Med.* 35, 760-7(1925).—"Hourly variations in the % of hemoglobin of the blood, which have been shown to occur in normal persons, do take place in anemia, though to a less extent. Hourly variations in the av. size of the erythrocyte may be considerable. A definite relation between the % of hemoglobin and the cell surface seems to exist in a certain % of the cases." I. GREENWALD

The production of acidosis by anoxemia. A. E. JOZEWLER, E. H. BRUNQUIST AND A. S. LOEVENHART. *J. Biol. Chem.* 64, 313-23(1925); cf. *C. A.* 17, 3364. I. G.

The carbohydrate metabolism of tumors. I. The free sugar, lactic acid and glycolytic content of malignant tumors. C. F. CORI AND GERTY T. CORI. *J. Biol. Chem.* 64, 11-22(1925).—"Spontaneous and transplanted mouse carcinoma and Jensen rat sarcoma showed at a normal blood sugar level of the tumor-bearing animals a free sugar content of 0.051% (av. of 16 expts.) and a lactic acid content of 0.031% (av. of 9 expts.). After glucose administration the free sugar concn. of these tumors rose to 0.228 and 0.254% (av. of 4 expts. each), and the lactic acid concn. to 0.137% (av. of 7 expts.). The glycogen content of 6 individual tumors was as an av. 0.196%." Cf. *C. A.* 19, 1013, 1164, 2242. I. GREENWALD

The surface tension of serum during and after pregnancy. LEDERER. *Klin. Wochschr.* 4, 1472(1925).—The surface tension of serum steadily decreases during pregnancy, reaches its lowest level at the time of delivery and rises rapidly to normal after delivery. The lowest values are obtained in eclampsia. MILTON HANKE

Chemical composition of cardiac muscle in different diseases. GERHARD DOMAGK. *Z. Klin. Med.* 98, 171-219(1924); *Chem. Zentr.* 1924, I, 1551-2.—The % of the total N present as coagulable protein is increased in cloudy swelling and decreased in induration and necrosis. The abs. amt. of coagulable protein is markedly increased in hypertrophy and decreased in atrophy. The residual N is increased in tuberculous caries of the bones, diabetes, fresh necrotic foci in the myocardium, acute yellow atrophy of the liver, and renal diseases with injury to the glomeruli and vessels; it is increased in nephroses (amyloid and lipoid) only if necrotic foci exist in the body. The fat content is increased in anemia and aortic insufficiency. The water content is increased in atrophy, and especially in tuberculosi. JOSEPH S. HEPBURN

The antitryptic action and its diagnostic value. B. PURJESZ, JA AND S. WEISS. *Wiener Arch. inn. Med.* 10, 377-92(1925); cf. *C. A.* 19, 1009.—A quant. method was worked out for the detn. of the antitryptic action of serum. Serum and egg albumin show a certain amt. of parallelism in their antitryptic action and the antitryptic action

of serum is presumably due to some protein, probably albumin. Serum heated to 56° loses its antitryptic action, and this may be due to the change of albumin to globulin.

HARRIET F. HOLMES

The influence of protein-free organ extracts in the animal organism. A. GIGON AND H. STUDER. *Z. ges. expil. Med.* 45, 654-68(1925).—Protein-free exts. prepd. from lung, liver and intestine, after the method for obtaining insulin, are toxic for mouse, rabbit and pigeon, but differ in effect. N metabolism is not affected by the ext. of intestine but with liver ext. there is a loss of N and with lung ext. a retention of N. Acute *beriberi* symptoms in pigeons are relieved for a few days by liver and lung exts., but not by intestine ext., indicating that *beriberi* is not wholly due to avitaminosis.

HARRIET F. HOLMES

The action of mechanically produced hyperventilation on the acid-base equilibrium. J. DUZÁR, J. HOLLÓ AND ST. WEISS. *Z. ges. expil. Med.* 45, 708-13(1925).—Mechanically produced hyperventilation of the lungs both in man and in dogs causes increased alkalinity of the blood with symptoms of tetany. Interchange between blood plasma, blood corpuscles and tissues plays an important role in the regulation of the reaction of the blood and of the CO<sub>2</sub> content in the blood plasma.

HARRIET F. HOLMES

Origin of cholesterol gallstones. K. ROSINOUKI. *Beitr. path. Anat.* 72, 456-74 (1924).—The cholesterol in the bile obtained from the ligated gall-bladder of the dog is only slightly diminished. The cholesterol is deposited in the epithelium of the mucous membrane of the gall-bladder and there is no evidence that there is a secretion of cholesterol. There is no definite connection between this cholesterol deposition in the mucous membrane and the formation of gallstones.

JULIAN H. LEWIS

Character of the Wassermann reaction. CARL PRAUSNITZ AND MARGARETE STERN. *Centr. Bakt. Parasitenk. I Abt.* 90, 246-60(1923).—If a mixt. of ext., syphilitic serum and complement is filtered through a thin layer of kieselguhr, after digestion for 1 hr. at 37°, an excess of serum or ext. can be detected by the addition of ext. and complement or serum and complement. If a mixt. that contains an excess of ext. or serum is filtered the filtrate also shows the excess and if a balanced mixt. is filtered the filtrate is also balanced. This is contrary to the ideas of Wassermann and Citron who believe that the filtration of the aggregate of ext.-serum-complement is split by the kieselguhr and the ext. adsorbed. If they were correct the filtration of const. quantities of serum with different quantities of ext. would always result in the same kind of filtrate. This was found not to be so. Complement should also be found in the filtrate. With strongly positive syphilitic sera this was never found; in weakly positive sera it was found only at certain concns.; and with normal sera it was found in all cases and in all concns. Filtration cannot be a "confirmation test," as proposed by Wassermann and Citron, because with certain concn. relations of ext. and syphilitic serum the filtrate does not show syphilitic serum, and cannot be differentiated from normal serum-ext. mixts. Simple shaking of the mixt. with kieselguhr and subsequent centrifugation produces the same effect as filtering. Under suitable conditions ext. and syphilitic serum occur simultaneously in the same filtrate because the filtrate alone bound added complement. The results of filtration are applicable for quant. detn. of the ext.-binding capacity of syphilitic sera. As complementary to the Wassermann reaction for those cases which in spite of sp. treatment are uninfluenced and with which the Wassermann test remains stubbornly positive, the filtration method is applicable.

JULIAN H. LEWIS

Studies in hypersensitiveness. XIII. A study of atopic reagins. A. F. COCA AND ELLA F. GROVE. *J. Immunol.* 10, 445-64(1925).—The atopic reagins, discovered by Prausnitz and Küster, have been found in the blood of all subjects of hay fever and asthma in whom the cutaneous reaction to the injection of the atopen is positive. Of normal skins 84% are susceptible to local passive sensitization; 11% are non-receptive and 5% are slightly receptive. Local passive sensitiveness lasts at least 4 wks. Heating for 0.5 hr. injures the atopic reagins. Normal human skin could not be passively sensitized with an anti-egg pptg. serum or an anti-ragweed pollen pptg. serum, both from an injected rabbit. The atopic reagin can be neutralized in the test tube or tissues. It does not produce a visible ppt. nor fix complement when mixed with the related atopen. The atopic reagin does not conform, in its successive fractional neutralization, with the quant. law governing the fractional neutralization of precipitin. The atopic reagin is unable to sensitize the guinea pig or guinea-pig uterus. It is sp. In the blood of persons sensitive to more than one substance more than one reagin can be demonstrated. Sensitizing substances could not be demonstrated with the method of Prausnitz and Küster in the blood of persons sensitive to tuberculin or poison ivy. XV. On the nature of the atopens of pollens, house dust, horse dander and the green

pea. ELLA F. GROVE AND A. F. COCA. *Ibid* 471-81.—The removal of all protein and other detectable nitrogenous substance from pollen and house dust exts by means of tryptic digestion and dialysis causes no appreciable lessening of the atopic activity of the exts; these atopens seem, therefore, not to be proteins. Tryptic digestion of horse dander and the green pea causes a diminution of atopic activity, corresponding with the loss of protein by digestion. These atopens seem thus to be protein. XVI. Antigens. A comparative study of the antigenic properties of pollens, egg white and glue in guinea pigs, as determined by the intravenous and Dale methods of testing in anaphylaxis. MATTHEW WALZER AND ELLA F. GROVE. *Ibid* 483-553.—Timothy and ragweed pollens have definite antigenic properties and may induce in the guinea pig a condition of hypersensitivity. Intravenous injection of the sp. antigen in such animals can cause death by acute or delayed anaphylactic shock. The pollen antigen-antibody reaction is much more time consuming than that of egg-white, both *in vitro* and *in vivo*. Precipitins have not been demonstrated in the pollen-sensitive animals. Digestion with trypsin and dialysis does not remove the antigenic principle of ragweed pollen. The non-digestible, non-dialyzable factor is common to both high and low ragweed pollens, and is almost as strongly antigenic as whole pollen. Beside the non-digestible, non-dialyzable factor, there are less important antigens in ragweed, probably protein in nature. E. R. LONG

Hepatic reactions in anaphylaxis. IX. Effects of dehepatization on the reactions of certain smooth muscle structures in canine anaphylaxis. W. H. MANWARING, V. M. HOSEPIAN, J. R. ENAIGHT AND DOROTHY F. POSTER. *J. Immunol.* 10, 567-74 (1925).—During the first 2 min. of typical anaphylactic shock in intact dogs, the uterus, urinary bladder and intestines are thrown into sharp contraction. These typical anaphylactic contractions do not take place on intravenous injection of sp. foreign protein into dehepatized anaphylactic dogs. Smooth muscle contractions, therefore, appear to be due to chem. products (hepatic anaphylatoxins) explosively formed or liberated by the anaphylactic liver, products having a histamine-like effect on smooth-muscle structures. X. The hepatic anaphylatoxin. W. H. MANWARING, V. M. HOSEPIAN, F. I. O'NEILL AND H. BING MOY. *Ibid* 575-81.—The immediate reactions between sp. foreign protein and anaphylactic blood are in themselves usually insufficient to cause recognizable anaphylactic phenomena in normal dogs. If the liver of an anaphylactic dog is transplanted into a normal dog, the normal dog will show all the characteristic features of canine anaphylaxis on intravenous injection with a sp. foreign protein. If sp. foreign protein is injected into a mesenteric vein of an anaphylactic dog and shock blood collected as it escapes from the liver, this blood, transfused into a normal dog, will reproduce all the characteristic features of canine anaphylaxis. Blood drawn from the carotid artery 2-5 min. after a dog is thrown into anaphylactic shock usually shows little or no toxic action in a normal dog. The hepatic anaphylatoxin is not the only factor operating in canine anaphylaxis. XI. Glycogen content of the anaphylactic liver. F. I. O'NEILL, H. BING MOY AND W. H. MANWARING. *Ibid* 583-5.—Glycogen disappears almost quant. from the canine liver during the first 15 min. of anaphylactic shock. E. R. LONG

The action of pancreatic extracts on complement. ARTHUR WORNALL, H. R. WHITEHEAD AND JOHN GORDON. *J. Immunol.* 10, 587-94 (1925).—Pancreatic exts. acting on whole guinea-pig serum first destroy the end piece or albumin fraction. If the reaction is allowed to proceed for a much longer period, both components of the complement are destroyed. In this way the destruction of the complement action of whole serum runs parallel to the destruction by heating to 56°. The isolated mid- and end-piece fractions are both rather rapidly destroyed by the enzyme exts., the latter being more resistant than the former. The greater resistance of the end-piece fraction is attributed to the presence in it of the anti trypsin present in the serum. E. R. LONG

The antigenic properties of extracts of horse dander. I. Active sensitization of guinea pigs to horse-dander extract. W. T. LONGCORE, D. P. O'BRIEN AND W. A. PERLZWEIG. *J. Immunol.* 10, 599-612 (1925).—Guinea pigs sensitized with horse dander die in acute anaphylactic shock when injected intravenously with ext. of horse dander, and the uterus of sensitized virgin guinea pigs respond and contract in a characteristic manner on the addn. of small quantities of the ext. to the Dale bath. Desensitization is possible. The sensitization of guinea pigs to horse dander is sp. E. R. L.

A study of agglutinable antigens of *Bacillus influenzae*. I. Methods of preparing and preserving antigens of *B. influenzae* and their effects upon specific agglutination. MARY J. EVANS AND J. C. SMALL. *J. Immunol.* 10, 613-24 (1925).—*B. influenzae* antigen is best prepd. by growing the bacteria on heated blood agar, washing off with saline, heating to 87° for 1 hr., making up in physiologic saline, and storing in the refrigera-

tor. When serum dilns. are made in beef broth at  $pH$  7.6, the agglutination results are much sharper than when either physiol. saline or Ringer soln. is used. The difference is not so marked when the antigen is especially sensitive. Aging and autolysis tend to render antigens less suitable for the agglutination reaction, and to make them prone to spontaneous, non-sp. clumping.

E. R. LONG

The specific substances in the alcohol extract of the bacillus of tuberculosis. L. DIENES AND E. W. SCHORNHEIT. *J. Immunol.* 10, 631-42(1925); cf. *C. A.* 18, 114.—Lipoidal exts. were obtained from tubercle bacilli, with  $Et_2O$ ,  $EtOH$  and  $MeOH$  as solvents, which were of almost equal value as antigens in the complement fixation test. The unit as a rule was found to be 0.00020-0.00030 mg. of the lipid prepn. Chemically the products appear closely similar. Carbohydrates are present in large amt. in the unpurified exts., and on purification 12-26% remains. The purified product differs widely in chem. compn from the well-studied phosphatides.

E. R. LONG

Observations on the specific part of the heterogenetic antigen. K. LANDSTEINER AND P. A. LEVENE. *J. Immunol.* 10, 731-3(1925).—Heterogenetic antigen isolated from horse kidney by the methods generally employed for the sepn. of lipoids led to the production of fractions chemically different as regards their N, P and S, but of approx. the same activity. Fractionation with neutral solvents often produces portions of high and low activity, the sum total suffering much loss. The strength of some prepsn. was increased by the addn. of crude ox brain sphingomyelin, which in itself had little or no activity in tests with heterogenetic antibodies. Active fractions were prepd. by a method of extn. with boiling alc., which were sol. in water, and insol. in ether, alc., acetone and  $CHCl_3$ . The soln. gave a negative biuret test. One sample analyzed as follows C 59.64, H 10.09, N 2.33, P 1.10, S 0.81, ash 4.22%. On hydrolysis with  $HCl$  the product yielded water-insol. acids and a reducing substance from which a dextro-rotatory osazone was obtained. With orcein the color test for galactose was given. The soln. reduced Fehling soln. only after hydrolysis.

E. R. LONG

Flocculation reactions with immune sera produced by injections of organ emulsions. J. VAN DER SCHEER. *J. Immunol.* 10, 735-9(1925).—The expt. concerned autoimmunization. The injection of emulsions of rabbit organs into rabbits produced serums capable of flocculating alc. organ exts. in several instances where no reactions were observed with the same serums before injection.

E. R. LONG

Intestinal autointoxication. W. C. ALVAREZ. *Physiol. Rev.* 4, 352-93(1925).—Review with extensive bibliography.

E. R. LONG

Theory of the Wassermann reaction. L. SILBER AND W. FRIESE. *Z. Immunitäts.* 42, 425-38(1925).—A paraffin suspension, prepd. by adding a satd. alc. soln. of paraffin to 5 vols. of physiol. salt soln., acted as antigen in the Wassermann reaction in the same manner as the usual lipid antigen, with both human syphilitic serum and positive rabbit serum. With rabbit serum, but not with human syphilitic serum, a prepn. of gelatin acted qual. and quant. like the usual antigen. The action of the antigen in the Wassermann reaction thus depends on physical factors and not on chem. structure.

E. R. LONG

Investigations on the specificity of the anti-urine serum. R. KAMEKURA. *Z. Immunitäts.* 42, 439-58(1925).—Rabbits treated with protein-contg. and protein-free urine develop precipitins for the serum proteins of the subject voiding the urine. Usually the rabbit antiserum causes a ppt. in the urine itself. No reaction is given with the serum or urine of other animals. The development of precipitins with normal urine probably depends on the presence of traces of protein.

E. R. LONG

The relation of serum lipoids to the protein fractions. KATE FRANKENTHAL. *Z. Immunitäts.* 42, 501-6(1925).—Normal serums were fractionated by salting out and by dialysis. The majority of lipoids come out with the globulin fraction. In 2 serums, one pptd. with  $(NH_4)_2SO_4$  and one subjected to electrodialysis, the entire cholesterol content came out with the globulin. In Wassermann-positive human serum, on the other hand, the majority of lipoids appear in the albumin fraction.

E. R. LONG

The pathogenesis of anaphylactic shock and related and similar processes. I. L. KRITSCHESKY AND K. A. FRIEDE. *Z. Immunitäts.* 43, 1-35(1925).—The following conditions result in qual. and quant. identical anatomic changes: active and passive serum anaphylaxis, active and passive cellular anaphylaxis, toxicity of hemolytic serums, primary toxicity of normal animal serums for animals of other species, toxicity of anaphylatoxin, toxicity of foreign erythrocytes, toxicity of organ exts., and toxicity of peptone and coteydon juice. In all these cases the toxic process is the result of a change in the dispersion of the protoplasm colloids. In parenchymatous organs and muscle fibers a decrease in the degree of dispersion of the protoplasm colloids occurs, and in the ganglion cells an increase.

E. R. LONG

The influence of different metal salts on hemolysis by tetanolysin and the inhibitory action of liver extract. LEO BLEYER. *Z. Immunitäts* 43, 70-8(1925).—The inhibitory action of liver ext on tetanolysin-hemolysis is not influenced by neutral salts. The hemolytic action of tetanolysin can be prevented or inhibited by the addn. of various neutral salts. No relation was observed between the atomic wt. of a metal and its ability to injure tetanolysin. On the other hand the position of a metal in the periodic system is important, group relationships being observed. Increase in the activity of tetanolysin through the addn. of salts was not observed. E. R. LONG

The irreversible thermolability of specific precipitates. FRITZ OTTENSOOSER. *Z. Immunitäts* 43, 91-4(1925).—Irreversible thermolability is probably a general property of sp ppts. On this and other grounds these ppts. can be looked upon as antigen-contg. lipoid-globulin ppts. E. R. LONG

*Aspergillus* protein as antigen. FRITZ OTTENSOOSER. *Z. Immunitäts* 43, 79-90 (1925).—In takadiastase the protein of *Aspergillus oryzae* can be recognized by immunological tests. Takadiastase does not react with yeast protein antiserum or animal protein antisera. By the precipitin reaction *Aspergillus oryzae*, *flavus* and *niger* can be sharply differentiated from yeast, but they give group reactions with each other. Antiserum to takadiastase reacts more strongly with *Aspergillus oryzae* than with the *flavus* and *niger* varieties. E. R. LONG

The Wassermann tuberculosis reaction and the lecithin flocculation test applied to cattle and calves. HELMUT WENDT. *Centr. Bakt. Parasitenk. I. Abt. Orig.* 94, 26-35(1925).—The Wassermann complement-fixation reaction for tuberculosis was not only positive for cattle with active tuberculosis but also with animals in which no pathology was found on section. It was always negative with calves. The Sachs-Klopstock lecithin flocculation test was not always parallel with the Wassermann. In bovine tuberculosis there is no relation between the globulin content of the blood serum and the lecithin test. JOHN T. MYERS

The influence of several oxidizing agents on tetanus toxin. G. WESSENBERG AND A. HOFFMAN. *Centr. Bakt. Parasitenk. I. Abt. Orig.* 94, 416-31(1925).—Tetanus toxin was completely removed from filtrates by salting out with  $(\text{NH}_4)_2\text{SO}_4$  without loss of potency.  $\text{H}_2\text{O}_2$  destroys its toxicity quickly, and kills tetanus spores slowly. One part  $\text{CaOCl}_2$  to 10 parts toxin destroys it in 5 min. JOHN T. MYERS

Antigens of red blood corpuscles. II. Flocculation reactions with alcoholic extracts of erythrocytes. K. LANDSTEINER AND JAMES VAN DER SCHEER. *J. Exptl. Med.* 42, 123-42(1925); cf. *C. A.* 19, 1310.—Flocculation reactions of anti erythrocyte sera on emulsions of alc. exts of blood are described; the reactions are markedly species-specific. Besides the homologous reactions certain others—"heterogenetic" ones (monkey blood immune sera-pig blood, horse blood immune sera-rat blood)—have been observed, and in this way the existence of new examples of heterogenetic antibodies has been demonstrated. Group specific substances can be extd. from human erythrocytes with  $\text{EtOH}$  and demonstrated by flocculation with group-specific immune sera. A conception of the structure of cellular antigens based upon the known facts is presented. C. J. WEST

Reducing power of normal and cancer tissues. C. VOEGTLIN, J. M. JOHNSON AND H. A. DYER. *J. Pharmacol.* 24, 305-34(1924).—The rates of reduction of equimol. proportions of certain dyes under standard anaerobic conditions by different normal and cancer tissues were compared. The most sensitive indicator for the process was found to be *m*-bromophenolindophenol. Blood plasma, serum, and the necrotic part of carcinoma tissue were found to possess no reducing power; all other tissues tested were able to reduce the dyes, the greatest activity being observed with liver, kidney and testis; the reducing power of actively growing carcinoma tissue is similar to that of normal tissue. The toxic effects following injection of dyes such as methylene blue can be, in part at least, abolished by simultaneous injection of glutathione but not by cysteine or thioglycolic acid, from which it is inferred that the function of glutathione may be the regulation of the equilibrium between oxidizing and reducing substances in the living cell. The rate of reduction of the dyes employed increases with an increase in their electrode potential. C. J. WEST

URBAIN, ACHILLE. La réaction de fixation dans la tuberculose. Paris. Masson et Cie. 132 pp. F. 12. Reviewed in *J. State Med.* 33, 319(1925).

## 11—PHARMACOLOGY

ALFRED N. RICHARDS

The mechanism of blood poisoning. WERNER LAPSCHITZ. *Ergebnisse Physiol.* 23, 1 Abt. 1-32(1924).—A review describing the chemical effects of poisons which act directly and indirectly on the blood. H. J. DEUEL, JR.

Arsphenamine-calcium therapy in non-tuberculous diseases of the lung. B. POCK. *Wien. klin. Wochschr.* 38, 118-21(1925) W. F. GOEBEL

The chemotherapy of organo-arsenic compounds. G. M. DYSON. *Chem. Age* (London) 13, 84-7(1925).—A review B. H.

Comparison of the effects on the isolated heating intestine of carbon dioxide and of a mineral acid. LOUIS MCP FRASER. *Am. J. Physiol.* 72, 119-24(1925).—Strips of rabbits intestine beating in physiological salt soln. show suppressed activity at  $p_{H}$  6.4 when the acid added is  $CO_2$ . With HCl there is usually no change in the tissue activity at  $p_{H}$  6.4, the beats becoming irregular or small at about  $p_{H}$  5.4. Recovery after exposure to  $CO_2$  is more rapid and complete than after HCl treatment. J. F. L.

## 1—ZOOLOGY

R. A. GORTNER

The effect of hydrogen-ion concentration on behavior, growth, and occurrence of *Spirostomum*. J. T. SAUNDERS. *Proc. Camb. Phil. Soc. (Biol.)* 1, 189-203(1924); *Physiol. Abstracts* 9, 570-1.—Details are given of the reactions induced in *Spirostomum* by altering the H-ion concn. of its environment. The death of *Spirostomum* caused by placing them in shallow water is not due, as Pütter thought, to O poisoning, but is caused by the  $p_{H}$  rising above the lethal value. The animals are positively tropic for water at  $p_{H}$  7.4, but only when in the light. H. G.

## 12—FOODS

W. D. BIGELOW AND A. E. STEVENSON

Determination of the alkalinity of ash in foods. J. TILLMANS. *Z. Nahr. Genussm.* 49, 203-70(1925); cf. C. A. 15, 1949.—Criticism of the work of Pyl (C. A. 16, 3516) and Pyl and Samter (C. A. 19, 864). Data are presented to show that the degree of heat applied in ashing greatly affects the alkalinity of the ash. FRANK E. RICE

A further improvement of the method for estimating fat with trichloroethylene as a solvent. J. GROSSFELD. *Z. Nahr. Genussm.* 49, 280-9(1925); cf. C. A. 18, 1759.—Unless the fat content of a substance is more than 10% any error through loss of solvent by evapn. is negligible. For butter, cheese, meat and other fat-rich substances an app. is described and illustrated by means of which the solvent can be removed from the digestion flask and filtered without much exposure to air. FRANK E. RICE

Determination of sulfur dioxide in foods. K. K. JÄRVINEN. *Z. Nahr. Genussm.* 49, 283-6(1925).—Detection: Into a 100-cc. Erlenmeyer flask put 10 g. of material (dried fruit), moisten with 10 cc. 2 N HCl. Close with a cork which holds a piece of KI-starch paper; warm on a  $H_2O$  bath if a color does not appear in 5-10 min. Detn.: In a 500-cc. flask place 25 g. well sliced fruit, 300 cc.  $H_2O$ , 5 g. marble in pieces, and 25 cc. HCl. Attach an upright condenser which leads to a receiver contg. 25 cc. 0.1 N I soln. After  $CO_2$  evolution has ceased, apply a flame and distil until about 100 cc. remains. This should occupy 2-3 hrs. in order to permit diffusion of  $SO_2$  from the material. Det.  $H_2SO_4$  in the distillate by the usual methods. Various modifications of this procedure were tried but found not to give good results. FRANK E. RICE

Utility of the Feder number for judging the moisture content of "Hackfleisch," "Schabefleisch," "Fleischbrühwürsten" and "Fleischkochwürsten" (special sausage-like products). W. KERF AND G. RIESS. *Z. Nahr. Genussm.* 49, 217-33(1925).—The Feder no. ( $H_2O$ :org. non-fat) (C. A. 7, 3170) was detd. on a large no. of samples of various kinds of sausage products by different analysts with good comparative results. Meat from normal cattle gave numbers always below 4. Hog meat was similar except that a few parts of the carcass ran higher. The flesh of poorly nourished and sick animals gave numbers above 4, in the same direction as if  $H_2O$  had been added. For beef sausage 4 is considered a fair limit, but 4.5 is recommended for hog sausage. Where these limits are slightly exceeded it is recommended that an investigation be made first to ascertain whether or not animals may have been used the meat of which was unobjectionable but abnormal in this regard. The Grossfeld procedure for detg. org.

non-fat  $\frac{1}{2}$  N  $\times$  6.25) (C. 11, 856) checks with the original method (100% -  $\frac{1}{2}$  fat -  $\frac{1}{2}$  ash -  $\frac{1}{2}$  H<sub>2</sub>O) unless a carbohydrate has been added to the sausage; in such a case the N  $\times$  6.25 value is to be used in calcg. the Feder ratio. The % of added water in beef sausage is obtained by subtracting from the % total H<sub>2</sub>O,  $4 \times \frac{1}{2}$  org. non-fat. Added H<sub>2</sub>O in some special sausages should be permitted, the amt. to be detd. in each locality by the custom of the honest manufacturers. Details of all methods of analysis are given, and a comprehensive list of references is appended. FRANK E. RICE

**Reductase test for milk.** CHM. BARTHEL. *Swensk Kem. Tids.* 37, 157-65 (1925) — The reduction of methylene blue in milk takes place in two stages; first the acids are used up by the bacteria, then some substance normal to milk reduces the dye. Bacteria-free milk reduces the dye if the acid is first removed. Citrate, which is constantly present in milk, may be the H donor. Na citrate added to acid-free milk intensifies the reduction property of milk. A catalyst is also necessary and the catalyst is probably an inorg. component. The application of the test to grading milk is discussed.

A. R. ROSE

**Organic phosphorus in milk serum.** B. PFYL AND W. SAMTER. *Z. Naturforsch.* 40, 253-62 (1925) — To 20 cc. of "tetraserum" (C. 1, 10, 864) add 0.1 N HCl until acid to Me orange, then 12-15 cc. Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>; boil to remove CO<sub>2</sub> and filter to remove CaC<sub>2</sub>O<sub>4</sub> and albumin. Cool in ice H<sub>2</sub>O and titrate to phenolphthalein, using 0.1 N NaOH. Add an equal vol. of 40% CaCl<sub>2</sub> neutralized to phenolphthalein. Titrate the mixt. to the phenolphthalein end point with standard alkali; 1 cc. N soln. is equiv. to 1 millimole (31 mg.) of inorg. P. Det. total P in the serum ash; the difference between this and inorg. P gives org. P. This was found to amt. to 93-140 mg. per l., or 10-15% of the total P of milk. The detn. of inorg. P above described was checked in some samples by methods employing magnesia mixt., also NH<sub>4</sub> molybdate; and org. P was checked by direct detn. after pptn. of inorg. P; good results were obtained. Prepn. of milk serum in other ways led to the conclusion that the above figures are correct. Upon standing some org. P seems to be transformed to the inorg. form; but boiling the milk does not change the proportion. Data show that the org. P cannot be attributed to slight amts. of dissolved casein. Importance of inorg. P as a source of P in animal nutrition is pointed out.

FRANK E. RICE

**The influence of some bacterial enzymes on the heat coagulation of milk.** WM. C. FRAZIER. *J. Dairy Sci.* 8, 370-89 (1925) — The bacteria which curdle milk upon heating are classified into those which bring about the curdling by means of acid alone, and those that produce a rennin-like enzyme, which takes part in the coagulation. The action of organisms of these groups is studied. The theories of rennin action, isolation and purification of rennin and influence of purified enzymes on heat coagulation are discussed.

J. C. JURRYENS

**Modification of cow milk for infant feeding.** E. GATES AND W. M. BILLING. *J. Am. Pharm. Assoc.* 13, 1015-20 (1924). — The most satisfactory modifying substances are lactose, NaCl, NaHCO<sub>3</sub>, KHCO<sub>3</sub>, and Na<sub>2</sub>HPO<sub>4</sub>. Ca salts are omitted although they are often used as modifying agents. For 4 oz. of milk it is suggested to add lactose 35 gr., NaCl  $\frac{1}{2}$  gr., NaHCO<sub>3</sub>  $\frac{1}{2}$  gr., Na<sub>2</sub>HPO<sub>4</sub> 10 gr., and KHCO<sub>3</sub>  $\frac{1}{2}$  gr.

L. E. WARREN

**A study of the organisms causing thickening of sweetened condensed milk.** P. A. DOWNS. *J. Dairy Sci.* 8, 344-69 (1925). — Organisms were isolated from fresh milk, condensed milk and powdered milk. A description of the procedure used in the thickening test is given. The organism isolated from samples of commercial milk was similar to the one described by Greig-Smith. Of the organisms which thicken sweetened condensed milk one variety was identical with a culture of *Staphylococcus pyogenes albus* I, from the Lister Inst. collection, except that *albus* would not thicken condensed milk. A second variety composed most of the cultures isolated from sweetened condensed milk. They differed from the first in that they did not reduce nitrates to nitrites. This organism corresponds very closely to the *Micrococcus lactis albidus*. Many organisms of common occurrence closely resemble these thickening organisms, and can only be distinguished by the thickening test. Some acid-producing organisms did not cause thickening, indicating that the production of acid alone is not responsible for the thickening. The thickening process seems to be caused by a rennin-like enzyme produced by the organism.

J. C. JURRYENS

**Notes on the chlorination of milk.** F. P. MINETT. *J. Roy. Army Med. Corps* 44, 116-8 (1925). — Cl (4% chlorinated lime giving 29.9% available Cl) added in quantities varying from 0.5 to 3 cc. per 100 cc. milk is of no value as a milk purifier, since though it prevents souring and clotting for a considerable time it does not destroy bacteria in milk.

A. T. CAMERON

The milks of the Gex region (France). CH. GRANVIGNE, GILLET AND DENIZOT. *Ann. fals.* 18, 331-5 (1925).—A large no. of analyses are tabulated and commented on. The av. compn found from 304 analyses, representing the production of over 3,100 cows from Oct to May, was: fat 40.25, total solids 134.5, non-fat solids 94.25 g. per l.

A. PAPINEAU-COUTURE

Carbonation of butter. M. J. PRUCHA, J. M. BRANNON AND H. A. RUEHE. *J. Dairy Sci.* 8, 318-29 (1925).—Treatment of the cream with  $\text{CO}_2$  caused a delay in souring, 2 hours at room temp., and several days at  $35^\circ\text{F}$ .  $\text{CO}_2$  applied at churning time, replacing the air above the cream, did not inhibit mold growth, nor did it measurably affect the germ life in the butter, which had acquired a sourish taste.  $\text{CO}_2$  applied to butter and stored in air-tight containers, completely inhibited mold growth, but in time undesirable flavors developed.

J. C. JURRENS

Removal of sulfurous acid from grape sirup. W. V. CRUESS AND E. W. BERG. *Ind. Eng. Chem.* 17, 849-50 (1925).—Sulfurous acid is the most suitable preservative for grape juice to be used for the prepn of grape sirup. In order to preserve the juice for several months at least 1250 mg.  $\text{SO}_2$  per l. added as  $\text{H}_2\text{SO}_3$  soln. or 1000 mg. added in the form of  $\text{K}_2\text{S}_2\text{O}_5$  is needed; 1500 mg. per l. should probably be used in com. practice. The rate of removal of  $\text{SO}_2$  by an air stream is approx. in proportion to the temp. of the liquid. Heating the air does not materially increase the rate of removal. Removal by steam applied at atm. pressure or under vacuum is the most rapid method of removal of  $\text{SO}_2$ . Under vacuum, the quality of the juice is injured much less than in the open, and this method is recommended for com. use. Sulfates increase considerably, but not to a serious degree, in juices preserved with  $\text{SO}_2$ .

L. W. RIGGS

The gas content and ventilation of refrigerated holds carrying apples. A. J. SMITH, E. GRIFFITHS AND E. A. GRIFFITHS. Dept. Sci. Ind. Research, Food Investigation Board, *Special Rept.* No. 21, 36 pp. (1925).—See "D. G. H.," C. A. 19, 2093. B. H.

Brown heart in Australian apple shipments. A. J. SMITH AND FRANK SMART, Dept. Sci. Ind. Research, Food Investigation Board, *Special Rept.* No. 22, 28 pp. (1925).—See "D. G. H.," C. A. 19, 2093.

E. H.

Canned-food containers. A study with special reference to the influence of the steel base on resistance to perforation. ANON. *Nat. Canners Assoc. Bull.* No. 22L, 296 pp. (1923).—A minute description is given of expts. and results obtained in service tests with foods canned commercially in containers made of Sn plate of known history, from the charging of the open-hearth furnace for the steel base through the various steps till the plate was finished. Every step in the manuf. of the steel, Sn plate and cans and in the packing of the foods was closely followed. The investigation was primarily a study of the influence of Ti in the manuf. of steel as a base for Sn plate for food containers; but at the same time the effects of Cu on the steel base and the affects of different wts. of Sn coating were also studied. The general conclusion is that the resistance of Sn plate to perforation depends on so many factors, some of which are entirely unknown, that it is impossible to predict the service value of any can or lot of plate, though complete data on the steel and coating may be available; no Sn plate made from any heat of steel, regardless of methods of manuf., chem. compn., or wt. of coating, gave service indicating a satisfactory soln. of the problem of perforation. Resistance of Sn plate to perforation was increased by addn. of Ti in the ladle in the manuf. of the steel and by increase in the wt. of the coating. It is influenced to a greater or less extent by furnace practice, chem. compn. of the steel with special reference to the content and segregation of P and S, and by other factors. No advantage or disadvantage was apparent from the use of Cu. Use of Si in the mold causes large waste in the manuf. of Sn plate and reduces the resistance to perforation. The factors which affect the resistance to perforation are apparently entirely unrelated to the discoloration of cans and contents.

A. PAPINEAU-COUTURE

Black discoloration in canned corn. ANON. *Nat. Canners Assoc. Res. Lab. Circ.* No. 9L, 8 pp. (1924); cf. C. A. 16, 1816.—Summary of results previously obtained and of subsequent investigations. Indications are that the most practical method of preventing "corn black" is to coat the interior of the cans with a special enamel contg. suspended ZnO. Results to date show this prevents formation of the black without giving up an appreciable quantity of Zn to the contents of the can. (Cf. next abstract.)

A. PAPINEAU-COUTURE

Special enamel for corn cans. G. S. BOHART. *Nat. Canners Assoc. Res. Lab. Circ.* No. 10L, 5 pp. (1924); cf. preceding abstract.—As a result of extensive preliminary trials, the following mixts. were selected for trials in large exptl. packs: cumar 10, ZnO 5; cumar 18, gutta-percha 4, ZnO 11; cumar 18, chicle gum 4, ZnO 11. The following also looks promising: carnauba wax 1, chicle gum 1, ZnO 1.  $\text{CCl}_4$  was used as

vehicle, the enamel as applied contg 5% total solids. It was sprayed on to the covers and dried about 40 min at 110° F. The coating can probably be improved by increasing the ratio of wax and gums to ZnO to at least 3:1 instead of 2:1, and also by increasing the drying temp up to possibly 300° F. From 0.1 to 13.3 mg. of Zn per can was found to have been dissolved from the coating, according to the wt. of the latter. If the can ends had each carried 9.6 mg Zn, the corn would have taken up not over 6 mg per can, and this could probably be substantially reduced by increasing the proportion of wax and gum to ZnO, and by drying at higher temp. A. P.-C.

Tomato products—pulp, ketchup and chili sauce. W. D. BIGELOW AND A. E. STEVENSON. *Nat Cannery Assoc Res Lab Bull* No 21L, 74 pp (1923).—Outline of their method of manuf and compn, with a detailed description of methods of analysis and a discussion of these in their relation to mfg. control. A. PAFINEAU-COUTURE

Solubility of glazes and enamels used in cooking (MONIER-WILLIAMS) 19.

Apparatus for pasteurizing milk or other liquids in bulk. L. S. PFOUTS U. S. 1,546,552, July 21

Treating flour, etc., with peroxides. E. C. SUTHERLAND U. S. reissue 16,116, July 14. See original pat. No 1,380,334, C. A. 15, 3349

Emulsion of mustard-seed oil. J. ALSBERG. U. S. 1,545,993, July 14. A stable homogeneous emulsion adapted for flavoring cake, candy, etc. comprises an excipient such as gum arabic and glycerol in H<sub>2</sub>O together with minutely subdivided particles of a flavoring material such as oil of lemon and oil of mustard seed

### 13—GENERAL INDUSTRIAL CHEMISTRY

HARLAN S. MINER

Industrial poisoning by aromatic compounds. D. H. KILLEFFER *Ind Eng Chem* 17, 820-2 (1925).—C<sub>6</sub>H<sub>6</sub> and its nitro, amino, chloro and azo deriva cause anemia, cyanosis and dermatitis. Preventive measures are demanded from efficiency as well as humanitarian standpoints. The prime essential is cleanliness, both of plant and employees. Follow-up of absences, exclusion of alc., warnings to employees, frequent medical exams, rotation of work and const medical attendance are necessary.

C. M. SALLS

Fusing refractory materials. C. O. FAIRCHILD and M. F. PETERS U. S. 1,545,931, July 14. Formation of carbide in the fusing of refractory materials such as oxides of Th or Zr is prevented by maintaining "an excessive oxidizing atm" during the fusing.

Annealing. T. F. BAILY. U. S. 1,546,532, July 21. Gas is circulated through hoods of high temp and through hoods of lower temp to raise the temp of material in the last mentioned hoods

Insulating materials. BRITISH THOMSON HOUSTON CO., LTD. Brit. 223,224, Oct 3, 1923. Asbestos board or similar fibrous sheet material is impregnated with petroleum wax tailings which had been modified by distn so as to raise its flow point to 45-50°.

Spray coating with liquids. W. H. ALLEN U. S. 1,546,357, July 21. Air, employed for spraying nitrocellulose lacquers or similar liquid coating compns., is satd. with solvent material before it is brought into contact with the liquid to be sprayed, in order to produce a more even coating.

Methyl bromide as a refrigerating agent. J. M. CHANDLER. U. S. 1,547,202, July 28.

### 14—WATER, SEWAGE AND SANITATION

EDWARD BARTOW AND G. C. BAKER

Filtration plant census, 1924. C. G. GILLESPIE *J. Am Water Works Assoc.* 14, 123-42 (1925).—Plants of the United States serving the general public and having a capacity of 1 million gal per day or more are listed. E. H.

Modern British practice in water softening. I. Theoretical considerations of the lime and soda-ash methods. D. BROWNIE *Ind. Chemist* 1, 303-5 (1925). II. A description of the lime water and soda-ash plants. *Ibid* 352-7. E. H.

Oxygen in river and lake waters. VALENTINO PETTINELLI. *Arch. farm. sper.* 39, 235-40 (1925).—Dets. of temp and dissolved  $O_2$  were made at monthly intervals during a year on samples taken from a depth of 0.5 m. from the River Tiber and Lake Bracciano. The  $O_2$  in the river  $H_2O$  followed regularly the expected variations due to differences in soly of the gas with seasonal variations in temp. In the lake  $H_2O$  the  $O_2$  content was greater than in the river  $H_2O$  during the spring and summer months, notwithstanding the fact that the av. temp was about  $2.5^\circ$  higher. The difference is explained by the greater activity of plankton and aquatic plants in the lake. A similar difference was noted in hourly observations during a 24 hr. period in August. The river showed a min. of  $O_2$  with a max. of temp, while the lake showed the max.  $O_2$  content at the max. temp.

A. W. DOX

Studies on the composition of sea water. C. B. LIPMAN. *Carnegie Inst. Washington Year Book* 22, 159 (1924). *Botan. Abstracts* 14, 23.—The compr. of sea water is apparently much more variable than has been thought. Some of its constituents that are generally overlooked may be of great ecological and physiol. importance. H. G.

Composition of the water of the Salton Sea. E. B. WORKING. *Carnegie Inst. Washington Year Book* 22, 66 (1924). *Botan. Abstracts* 14, 24.—An analysis of water collected in June, 1923, is presented. There has been but little decrease in the vol. of the Salton Sea since 1919.

H. G.

Some further notes on cresol as a larvicide. J. E. M. BOYD. *J. Roy. Army Med. Corp.* 44, 285-7 (1925).—Solns. of 1:100,000 will destroy larvae. Lesser concns. are uncertain.

A. T. CAMERON

Disinfection of rooms with formalin vapor. D. REYNOLDS. *J. Roy. Army Med. Corps* 45, 48-51 (1925).—Two pints of formalin and 2 lbs. of chloride of lime are necessary for each 1000 cubic feet. The room should remain closed for 24 hrs., and a gas mask is necessary when the room is opened. The treatment destroys bed-bugs and their ova.

A. T. CAMERON

Purifying water. S. V. H. LASSEN and UNITED WATER SOFTENERS, LTD. *Brit.* 229,239, Oct. 31, 1923. Mech. features of handling regenerating solns. for regenerating base-exchanging material.

Water filter. A. M. CAPRA. U. S. 1,546,199, July 14.

Softening water. A. N. FINN. U. S. 1,547,111, July 21.  $H_2O$  is treated with  $MgO$  to decompose bicarbonates and with  $BaCO_3$  to effect pptn. of sulfates and reaction with alkali salts to transform them into carbonates.

Apparatus for softening water by chemical treatment. R. O. FRIEND. U. S. 1,548,374, July 21.

Apparatus for precipitating scale-forming substances from boiler feed water. D. R. YARNALL. U. S. 1,546,960, July 21. A boiler is connected with a precipitator which is provided on its exterior with heat-radiating ribs and on its interior with throttling devices, which serve to control the circulation of  $H_2O$ .

## 15—SOILS, FERTILIZERS AND AGRICULTURAL POISONS

J. J. SKINNER

Energy transformation by microorganisms and the application of this phenomenon to soil processes. S. A. WAKSMAN. *Abstracts Bact.* 9, 31-2 (1925).—A general discussion showing the value that will result from considering chemical changes in soil from the viewpoint of energy supplies for the organisms responsible for them.

F. W. TANNER

What organism is responsible for the decomposition of cellulose in the soil? C. E. SKINNER. *Abstracts Bact.* 9, 32 (1925).—Fungi are the main organisms decomposing cellulose in the soil. Species of *Fusarium*, *Trichoderma*, *Penicillium* and *Alternaria* are most important. Elimination of these fungi by  $CS_2$  treatment was followed by little or no decompn. of cellulose.

F. W. TANNER

The use of *Azotobacter* as a test for the lime requirement of soils. P. L. GAINES. *Abstracts Bact.* 9, 29-30 (1925).—Soils more acid than  $pH$  6.0 do not contain *Azotobacter*. Soils less acid than this almost always contain it. To det. whether a soil is more or less acid than this, mannitol culture soln. can be treated with a small quantity of the soil in question and the type of growth observed. Treatment of an acid soil inoculated with *Azotobacter* with varying quantities of  $CaCO_3$  permits the detn. of the quantity of  $CaCO_3$  required to reduce the acidity of any given soil.

F. W. TANNER

Modern methods in the manufacture of superphosphate in America. B. COLBY and J. T. JONES. *Techn. Tids* 55 (Kem. afd. 6) 30-2, 39-40 (1925). A. R. ROSE

Fertilizer. J. BRESLAUER and C. GOUDRY. U. S. 1,546,562, July 21. An  $\text{NH}_4$  salt such as  $\text{NH}_4\text{NO}_3$  is mixed with raw  $\text{CaCN}_2$  in sufficient quantity to neutralize the free lime present, without loss of N, thus producing a fertilizer material contg. approx. the same proportion of N as the original raw cyanamide.

Treating phosphate rock. G. SINGLETON. U. S. 1,546,946, July 21. Phosphate rock contg. carbonate is heated sufficiently to eliminate org. matter while at the same time  $\text{CO}_2$  is retained so that the material is suitable for making acid phosphate.

Insecticide. W. C. JONSON. U. S. 1,546,240, July 14. A soln. adapted for use on plants is formed of nicotine sulfate, creosote, lime,  $\text{NaCN}$  and  $\text{H}_2\text{O}$ .

Organic mercurial insecticides. A. KLÄGER and SACCHARIN-FABRIK, AKT. GES. NORM. FAHLBERG, LIST & Co. Brit. 228,595, Oct. 10, 1923. Alkali salts of hydroxy-mercuriphenols are prep'd by treating solns. of alkali salts of phenol or its homologs with freshly pptd.  $\text{HgO}$  and evap'g to dryness *in vacuo*. The products are stable but their stability may be further increased by adding to the solns., before evap'g., salts such as alkali sulfites or cyanides, which are capable of reaction with the  $\text{-HgOH}$  groups. The products are adapted for treating seeds, etc.

## 16—THE FERMENTATION INDUSTRIES

C. N. FREY

Determinations and calculations of the distillation curve of ethyl alcohol-water. E. ÖMAN and A. GUNNELIUS. *Techn. Tids* 55 (Kem. afd. 5), 34-8 (1925).—Detns. are made of the b. p. of alc. in water solns. The table gives the temps. for each % from 1 to 100 including 0.5%. Variations in the detns. were reduced to 0.01° and the probable error is given as  $\pm 0.02$ . The lowest temp. is 78.04° for 95.5-96% alc. From the b. ps. the alc. content of vapors from boiling solns. are calcd. The method is briefly: the concn. of the soln. is known and the b. p. ascertained from the table; by knowing the b. p. the vapor pressure of  $\text{H}_2\text{O}$  may be known; from the mol. % of the  $\text{H}_2\text{O}$  in the soln. calc. the partial pressure of  $\text{H}_2\text{O}$  and get the partial pressure of the alc. by difference; partial pressures times mol. wts. give resp. wts. from which the % is calcd. The median mol. wt. of alc. in the vapor has been detd. as varying 0.255 per 1.0%, that for 95.6% being 18.75 and for 100%, 43.15. The points of the alc.- $\text{H}_2\text{O}$  distn. curve as calcd. are compared in a table with those exp'tly. detd. by Bergström (Swedish book distn.). The two are in close agreement. A. R. ROSE

Manufacture and properties of absolute alcohol. P. LORLETTE. *Mem. poudres* 21, 386-95 (1924).—Discussion of the fitness of alc.-gasoline mixts. for use as motor fuel. Attempts to dehydrate mixts. of gasoline with ordinary alc. in the cold by means of  $\text{Ca}$ ,  $\text{CaCl}_2$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{CaO}$ ,  $\text{CuSO}_4$ , etc. gave products which were stable only above  $-10^\circ$ . Satisfactory abs. alc. (99.9%) was obtained by dehydrating ordinary alc. in the vapor phase by distg. through a column of  $\text{CaO}$ . Fifteen parts of this mixed with 85 parts of gasoline gave a mixt. which remained homogeneous under conditions of humidity far more severe than would be encountered in practice. T. L. DAVIS

Some applications of the titration of polypeptides and amino acids by means of formaldehyde. ANTHELME VISEZ. *Bull. assoc. école sup-brasserie Louvain* 25, 166-74 (1925).—Digestible N in brewery by-products is generally obtained by the difference between total N and residual N after treating with pepsin at 37-40° for 48 hr. V. suggests  $\text{CH}_2\text{O}$  titration of the products of proteolysis, the progress of the reaction being followed by means of the ratio of total N to amino N. Aging of soft cheese is a function of the peptonization of the  $\text{Ca}$  salt of paracasein, and is therefore closely associated with the formation of free amino acids by proteolysis by molds and bacteria. Its progress can therefore be followed by  $\text{CH}_2\text{O}$  titration. The causes of the production from certain malts of beer highly sensitive to cold can also be studied by means of the  $\text{CH}_2\text{O}$  titration by following the effects of treatment with albumin, of boiling in presence of hops, of different strains of yeasts, and comparing the effects of treatment with malt ext. and pepsin, or comparing treatment with different acids. Results of preliminary tests indicate that the proteolytic enzymes break up the coagulable and insol. N, and in some cases give more amino acids than polypeptides, that the amino acids content decreases during fermentation, and that any proteolytic decompn. can easily be followed by this method. A. PAPINEAU-COUTURE

**Effect of adding the hops in the mash-tub.** J. RAUX *Brasserie et malterie* 15, 113-6(1925).—Several breweries consistently have obtained excellent results by opening up the hops and adding to the mash in the mash-tub, the lupulin being added in the brew kettle. Two cases are discussed in which addn. of the hops in the mash tub resulted in the production of a beer which was quite flat and lacked body and life. Lack of bitterness is attributed to insufficient cooking of the hops because the latter had not been sufficiently opened up and the bitter resins had been mostly retained in the spent grain. Loss of mellowness and foaming qualities is attributed to pptn. of colloidal albuminoids by the tannin of the hops, with consequent retention in the spent grain. This same pptn. probably occurs when the hops are added in the brewing kettle; but the ppt. is probably re-emulsified by the prolonged boiling. The stage at which the hops are added to the mash-tub probably is of considerable importance. A. P. C.

**Effect of the method of conducting fermentation on the stability of the foam, carbon dioxide content and stability of beers.** KALK *Wochschr. Brauw.* 45, 79 (1925); *Brasserie et malterie* 15, 117-23(1925).—A detailed discussion. A. P. C.

**Determination of the carbon dioxide content of beer and of the stability of the foam.** KALK. *Wochschr. Brauw.* 45, No. 13(1925); *Brasserie et malterie* 15, 123-6(1925).—The  $\text{CO}_2$  content is detd. approx. by pouring beer from a sepg. funnel into a beaker under specified conditions (technic described in detail), the height of the foam being proportional to the  $\text{CO}_2$  content and practically unaffected by the stability of the foam. The latter is judged from the appearance of the foam in the beakers after a given time. The test is useful especially for comparison of similar beers. A. P. C.

**Comparative analyses of red "drop" wines ("vins de goutte") and press wines from different wine cellars.** E. HUGUES. *Ann. fals.* 18, 347-53(1925).—Analyses are tabulated, with comments which bring out the variations in compn. of these two classes of wine obtained from the same vineyard. The press wines showed higher total solids, tannin, ash, total N, ammoniacal N,  $\text{P}_2\text{O}_5$ ,  $\text{SO}_2$  and Cl, the contents of these being higher in wine from second pressing than from first pressing. The alk. of the ash of press wines is relatively low. With normal vinification, there is but little difference in alc. content (not over 0.3% by vol.). Total and free tartaric acid, fixed acidity and total  $\text{K}_2\text{O}$  varied very irregularly. No reasons are advanced to explain the causes of the variations observed. A. PAPINEAU-COUTURE

**The wines of the 1924 vintage in Loir-et-Cher (France).** FALLOU. *Ann. fals.* 18, 353-8(1925).—Analyses of 45 wines are tabulated and commented on. A. P. C.

**Yeast.** A. P. C. JORGENSEN and N. L. C. H. KALHAUGE. *Brit.* 228,734, March 14, 1924. Molasses for cultivation of yeast is hoiled with  $\text{H}_2\text{SO}_4$  and superphosphate, powdered slaked lime is added and the liquid after standing is decanted and inoculated with lactic acid bacteria which have been especially acclimatized to molasses soln. When the lactic acid produced reaches the equiv. of 5 cc. *N* NaOH soln. per 100 cc. of the molasses soln., the soln. is sterilized and filtered. The ppt. obtained in clarifying the molasses is stirred with  $\text{H}_2\text{O}$ , which is then passed to a vat for yeast propagation with aeration and seeded with 15-30% of yeast. The acidified molasses is gradually added, with the addition of phosphatic and nitrogenous nutrients, with or without addition of a cereal wort.

**Acetone and butyl alcohol by fermentation.** I. W. WATERS U S 1,546,694, July 21. *Bacillus aceto-butylicum* is used to ferment a sugar mash contg. vegetable protein material readily assimilated by the bacillus, e. g., a mash formed from a cereal material and molasses. Corn gluten is preferably used.

**Denatured alcohol.** C. I. ROBINSON U S 1,545,927, July 14. Alc. is denatured with dil. acid-insol. products resulting from the treatment of olefin-contg. gases with  $\text{H}_2\text{SO}_4$  of a sulfating strength and kerosene

## 17—PHARMACEUTICAL CHEMISTRY

W. O. EMERY

**Iodoform gauze.** P. SCHÖTZL. *Pharm. Ztg.* 70, 935-6(1925).—The results of the examn. of some 36 samples of this product are recorded. W. O. E.

**Hydrogen-ion studies. XI. Preparation of dry antitoxin and agglutinin powders.** EDWIN F. HIRSCH. *J. Infectious Diseases* 34, 390-4(1924); cf. C. A. 18, 1332.—The ppt. obtained from antitoxin and agglutinating sera with  $(\text{NH}_4)_2\text{SO}_4$ , NaCl and dil. acids contain, when dried as a powder, the immune substances in a highly concd. form. An

antitoxin unit is contained in 0.35-0.38 mg. of the powder and agglutination has been obtained with mixts. of homologous bacteria in dilns. containing as little as 0.0035 mg. and 0.0022 mg. of dry wt. per cc. These powders are easily sol. in  $H_2O$  and have great stability.

JULIAN H. LEWIS

Detection of *Atractylis gummifera* in liquorice extract. P. BERTOLO. *Giorn. chim. ind. applicata* 7, 12-4 (1924).—B. defends his previous article (*C. A.* 17, 3747) against the criticisms of Giuffrè (*C. A.* 19, 1929). Giuffrè's method is complicated and gives unreliable results. He bases it upon the extn. and purification of the active principle of *Atractylis gummifera*, and the subsequent decompn. of this into valeric acid and atractyligenin. Since Giuffrè limits himself to identify the first by its odor, and the second by a color reaction (Anghico's), the results are not certain. Valeric acid may originate from other substances of a vegetable nature, e. g. angelica, asaetida resin, as well as from valerian root; while the color reaction for atractyligenin is not specific. B.'s method is more reliable, since it depends upon the identification of the sulfonic group in the active principle of *A. gummifera*. ROBERT S. POSMONTIER

Antiphymia. ANON. *J. Am. Med. Assoc.* 85, 535-6 (1925).—This nostrum is essentially a soln. of  $SO_2$  contg. some  $H_2SO_4$ . It is recommended by its manufacturers for the treatment of a variety of diseases, including tuberculosis. L. E. WARREN

An experiment in extraction. E. F. KELLY AND J. C. KRANTZ, JR. *J. Am. Pharm. Assoc.* 13, 815-8 (1924).—The objectives are to decrease the amt. of menstruum and to increase the amt. of extractive. A long narrow percolator is used and a modification of the Squibb repercolation method is employed. For 100 g. of drug the first 25 cc. is reserved. Three portions of 25 cc. each are collected as stronger percolates nos. 1, 2 and 3. These are added to the drug in the order named and 3 portions of 25 cc. each are collected as weaker percolates nos. 1, 2 and 3. These are added in the order named and 75 cc. is reserved as finished percolate. This is added to the first 25 cc. collected. Three drugs of known value were percolated by this method. Belladonna leaves yielded 72.1, aconite root 55 and podophyllum 69% of their active principles. Other carefully checked expts. showed that the marc contained some alkaloid after the displacement method had been completed. Three fl. exts. of belladonna leaves were prepd. by the U. S. P. method. From 190 to 200 cc. of menstruum was required for full extn. of 50 g. of drug. The exhausted drug was dried, the calcd. quantity of atropine- $H_2SO_4$  was dissolved in 10 cc. of EtOH and the soln. sprinkled on the drug. After drying, the drug was percolated. An av. of 183 cc. of menstruum was required for complete extn. The fl. exts. so prepd. pptd. a large quantity of extractive matter within a few days. The process was repeated and 155 cc. of menstruum required for complete extn. The mares were impregnated with free alkaloid and the extn. completed as before. The results were similar to those obtained with atropine- $H_2SO_4$ . The fresh marc required almost as much EtOH for extn. as the original drug but the succeeding extns. required less and less. The tests were repeated with Na sacchylate as the active principle. The first extn. required 170 cc., the third and fourth only 155 cc. Theories for the failure of this form of displacement are discussed. L. E. WARREN

Some observations on glycerol suppositories. W. L. SCOVILLE. *J. Am. Pharm. Assoc.* 13, 818-21 (1924).—Suppositories made by the official formula are of fair consistence but are opaque. Most commercial suppositories are transparent or translucent. Transparency can be produced by increasing the  $H_2O$  content of the U. S. P. formula but the product is too soft. Adding more Na stearate also increases the softness. An excess of alkali insures complete sapon and promotes transparency. A proper balance between the alkali and  $H_2O$  secures the best results. The mass should not be heated above the temp. of the steam bath but the heating should be continued with occasional vigorous stirring until the  $CO_2$  is driven out and the mass becomes clear. This promotes transparency. L. E. WARREN

The standardization and stabilization of aconite preparations. H. E. SWANSON. *J. Am. Pharm. Assoc.* 13, 1108-12 (1924); cf. *C. A.* 18, 882.—Tinctures prepd. with 70% EtOH, to which a little HCl or  $H_2C_4H_7O_2$  had been added before bottling, either retained their activity or deteriorated but slightly. Preps. which had been prepd. by adding a little acid to the menstruum before percolation were practically stable. Pharmacologic tests indicated that aconitine is about 10 times as toxic as diacetylaconine, 500 times as toxic as benzoylaconine, and 5000 times as toxic as aconine. Deterioration of aconite preps. may be prevented by adding an acid to the finished percolate or menstruum. The pure alkaloids do not hydrolyze in an acid EtOH medium. The deterioration of galenical preps. of aconite is probably due to the hydrolysis of the alkaloids. L. E. WARREN

A phyto-pharmacological method of assaying digitalis. D. I. MACHT AND J. C.

KRANTZ, JR. *J. Am. Pharm. Assoc.* 13, 1115-7(1924).—The effects produced by the galenical preps. of digitalis on the growth of plant seedlings were compared with the toxicity of the same preps. as detd. by the cat method. The seedlings used were *Lupinus albus* grown in Shive soil mixed with an equal vol of  $H_2O$ . The toxicity to seedlings runs a close parallel to the toxicity to the cat. L. E. WARREN

The alkalinity of magma magnesiae as determined by the hydrogen electrode. II. R. B. SMITH AND P. M. GIESY *J. Am. Pharm. Assoc.* 13, 1118-9(1924); cf. *C. A.* 18, 882.—Redetns. of the  $pH$  value for pure magma magnesiae confirm the earlier findings and show that the value lies between 10.51 and 10.54. The U. S. P. test for free alkalinity is unreliable. The electrometric method is much more delicate. III. The effect of magnesium carbonate. *Ibid.* 1119-20.—Although purified magma magnesiae has been obtained by washing the ppt. with  $H_2O$ , the  $pH$  value constantly becomes less with more washing while the sol. matter reaches a stationary point. It was suspected that the presence of an excess of  $MgCO_3$  might be responsible. To test the supposition a specimen of magma magnesiae was washed until its  $pH$  value became 10.52. An excess of  $MgCO_3$  was stirred in and the mixt. allowed to stand overnight. Its  $pH$  value was then found to be 10.18. The value was not lowered as much as was expected. L. E. WARREN

A study in the extraction of nux vomica. J. A. PIERCE *J. Am. Pharm. Assoc.* 13, 1128-9(1924).—The addition of 1%  $H_2C_2O_4$  to the U. S. P. IX menstruum for extg. nux vomica materially decreases the quantity of menstruum required for complete exhaustion but does not sufficiently reduce the quantity of fat extd. to make the method of value from this standpoint. The quality of the product is not lowered. L. E. WARREN

Bio-assay of veratrum preparations. L. W. ROWE *J. Am. Pharm. Assoc.* 14, 24-5(1925).—White mice have several advantages over frogs in the bio-assay of veratrum preps. The no. required is smaller, the time necessary is shorter and the method less expensive and more practical. The M. L. D. of an av. fl. ext. of *Veratrum viride* administered intraperitoneally is 0.0025 cc. per g. of body wt. of mouse. The method is as accurate as the frog method. L. E. WARREN

The educational value of a medicinal-plant garden. C. J. ZUFALL *J. Am. Pharm. Assoc.* 14, 26-8(1925).—From the pharmacognosy teacher's standpoint many practical applications of the medicinal-plant garden are pointed out. L. E. WARREN

A pharmacognostic and chemical study of ma huang (*Ephedra vulgaris* var. *Helvetica*). K. K. CHON *J. Am. Pharm. Assoc.* 14, 189-94(1925).—The histology of the plant is described in detail with illustrations. The active principle is an alkaloid, ephedrine. The alkaloid was extd. by percolation with 80%  $EtOH$ , evapn. of the solvent, and extn. with  $CHCl_3$  in the presence of  $NH_4OH$ . The alkaloid was converted into its  $HCl$  salt and crystd. 3 times from  $EtOH$ . Its salts crystallize well. Ephedrine m.  $210^\circ$ ;  $HCl$  salt, m.  $214^\circ$ ,  $[\alpha]_D^{20}$  in  $H_2O$   $-35^\circ$ ;  $H_2SO_4$  salt m.  $242^\circ$ . It is pptd. by the usual alkaloidal reagents. With  $H_2SO_4 + K_2Cr_2O_7$  it gives a bluish green color, which turns brown. Assays of 3 specimens gave from 0.019 to 0.030% of alkaloid. The moisture detns. showed about 4.6% and the ash about 8.4%. The ash contained the usual constituents. L. E. WARREN

The anatomy and botanical position of miré. H. W. YOUNGKIN *J. Am. Pharm. Assoc.* 14, 195-200(1925).—Microscopical examn. of the leaf and stem of miré show a striking similarity of structure to that of *Brunfelsia hydrangeaformis* Pohl, specimens of which were obtained from mucums. The histology of the rhizome and aerial stems is given in detail with drawings. L. E. WARREN

*Castela nicholsoni*, Hooker, Simarubaceae. Botany, pharmacology, and therapy. ALBERT SCHNEIDER *J. Am. Pharm. Assoc.* 14, 201-9(1925).—*Castela nicholsoni*, known as *Chaparro aviargosa* is reputed to be valuable in the treatment of amebic dysentery. The toxicity to frogs of a detannated and degummed dry. ext. of the plant was compared by Miss G. Sprecher to the toxicity of emetine- $HCl$ . The latter was about 20 times as toxic. The ext. is very bitter. Alkaloids were absent. Small quantities of oil,  $CaC_2O_4$ , reducing sugar and mucilage were present. Starch is sparingly present in the stems; more abundant in the roots. Ash 7.4%. Resin and chlorophyll were found. From reported clinical trials S. believes the drug to have therapeutic promise. L. E. WARREN

A palatable cod-liver oil concentrate possessing the therapeutic properties of cod-liver oil. H. E. DUNN *J. Am. Pharm. Assoc.* 14, 215-9(1925).—The method involves extn. of the oil with an org. acid, such as  $HCl$ ,  $H_2O_2$  or  $HCO_2H$ . The ext. is freed from acid and the remaining oil (about 5%) is saponified with alc.  $KOH$ . The soaps are dried and extd. with  $Et_2O$ . The solvent is evapd. and the residue dried in

absence of O. From 1000 g. of oil about 0.1 g. of ext. is obtained. Feeding expts. indicate that 0.1 g. of this ext. is as potent in antirachitic vitamin as 1000 g. of the original oil. The concentrate is a brown, semi-cryst., pasty mass. By mixing with sugar or other diluents it may be made into tablets. L. E. WARREN

Some physical constants of acetylsalicylic acid. J. L. HAYMAN, L. R. WAGNER AND E. F. HOLDEN. *J. Am. Pharm. Assoc.* 14, 388-92(1925).—Tests were made for salicylic acid according to N. N. R. The m. p., the second and third m. ps. after congealing, and the m. p. after crystal from various solvents were detd. The m. p. of 6 samples ranged from 129° to 131° (corr.). The purity of these samples was detd. by titration to range from 99.43 to 99.88%. The first second and third m. p. of one specimen were 132.5°, 128° and 126.5°, resp. A specimen of which the original m. p. was 134.8°, m. at 134.5° crystd. from  $\text{CHCl}_3$ , 134.3° from  $\text{C}_6\text{H}_6$ , 133° from  $\text{CCl}_4$ , 135.8° from acetone and at 135.0° from  $\text{EtOH}$ . The crystals from the several solvents have the same optical properties and cryst. form. In reporting the m. p. of acetylsalicylic acid it is necessary to give the method. L. E. WARREN

The disinfectant action and toxicity of trichloroisopropyl alcohol. J. W. HOWARD AND F. D. STIMPERT. *J. Am. Pharm. Assoc.* 14, 487-9(1925).—Bacteriological tests show that trichloroisopropyl alcohol has about 12 times the disinfectant power of isopropyl alcohol. Toxicity studies by injection into the abdominal region of guinea pigs showed that the substance is much more toxic than isopropyl alcohol. L. E. WARREN

Loss on ignition of talc. J. L. MAYER. *J. Am. Pharm. Assoc.* 14, 587-8(1925).—The U. S. P. IX states that talc when heated to redness loses not over 5% of its wt. A controversy having arisen over an analysis of talc, the substance was heated with different styles of burners both in Pt and porcelain dishes. Porcelain dish + Meker burner loss 2.68; porcelain + Bunsen burner loss 0.93; Pt dish + Meker loss 2.80; Pt + Bunsen 0.87; Pt + Meker improperly used 1.55%. The crucible should be placed about 2 mm. above the grid in the Meker burner to insure best results. L. E. WARREN

A partial analysis of the fruit of *Eupatorium urticaefolium*. F. S. BUKEY. *J. Am. Pharm. Assoc.* 14, 595-9(1925).—The cleaned fruit grown in Ohio was ground to pass a no. 60 sieve. The ground, dried drug was extd. with benzine and the exhausted marc dried at 105° and weighed; loss 17.35%. The oil by the benzine extn. was a dark, greenish brown, viscid substance which solidified at -24°. Insol. in cold  $\text{EtOH}$ ; sol. in  $\text{CHCl}_3$ ,  $\text{Et}_2\text{O}$ ,  $\text{C}_6\text{H}_6$  and  $\text{CCl}_4$ ; d<sub>4</sub> 0.9116, n<sub>D</sub><sup>20</sup> 1.475; I no. 145.3-155.2; sapon no. 157.3-163.21; insol. fatty acids 95%; solidifying pt. of fatty acids was -23°. The oil had drying properties. Fruit,  $\text{H}_2\text{O}$ -sol., 32.63; loss on drying 5.30; ash 8.82;  $\text{H}_2\text{O}$ -sol. ash 4.4%. The ash contained Cl,  $\text{SO}_4$ ,  $\text{P}_2\text{O}_5$ , K and Al and  $\text{SiO}_2$ . The Al amounted to 2.5%  $\text{Al}_2\text{O}_3$ ; crude protein 24.9%, crude fiber 20.36%. The toxic properties may be due in fact to Al compds. L. E. WARREN

Assay of Minnesota and other samples of digitalis. E. I. NEWCOMB AND E. B. FISCHER. *J. Am. Pharm. Assoc.* 14, 669-73(1925).—Minnesota-grown digitalis is reasonably uniform in activity from year to year. The av. M. L. D. of *Digitalis purpurea* grown in 1922 by the intravenous cat method was 77 mg. per kg.; in 1923 76 mg. per kg. and in 1924 72 mg. *Digitalis lutea* compares favorably with *D. purpurea* but it is doubtful if it has any distinct advantages over the latter. Studies are being continued in quest of a method for estg. the therapeutic value of digitalis by pulse reduction in the cat test. L. W. WARREN

Isopropylallylbarbituric acid. FARBWERKE vorm MEISTER, LUCIUS & BRÜNING. Brit. 228,195, Jan. 26, 1924. An alkali compd. of isopropylbarbituric acid is treated with an allyl halide either under pressure or at a raised temp.

Sodium magnesium sulfate. E. G. DAWSON and J. F. ROLLAND. Brit. 228,319, Jan. 3, 1924.  $\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ , a dry non-caking aperient salt, is prepd. from its components.

Oil emulsions of bismuth salts. G. T. COURT and W. KARRER. U. S. 1,547,167, July 28. Bi salts of fatty acids such as the oleate, tartrate or linolate are dissolved in ether or other volatile org. solvents, the soln. thus formed is mixed with an oil, e. g., olive or almond oil, and the volatile solvent is then removed by distn. The resulting products are suitable for injection as therapeutic agents.

## 18—ACIDS, ALKALIES, SALTS AND SUNDRIES

FRED C. ZEISBERG

Diosmosis of lemon juice. GUIDO AJON. *Giorn. chim. ind., applicata* 7, 17-20 (1924).—This article treats of the diffusion through a porous wall of the citric acid contained in lemon juice. In order to have a satisfactory sepn., the diosmosis should take place at ordinary temp., or at a temp. not high enough to alter the qual. compn of the juice. The curve of concn. of the aq. soln. of citric acid obtained from the juice by diosmosis through a porous wall, plotted with respect to time, is of a logarithmic character. The first part of this curve, however, compared to the rest, is anomalous.

ROBERT S. POSMONTIER

History of the saltpeter industry in the 18th century. P. MARTELL. *Z. ges. Schiess-Sprengstoffw.* 20, 65-9(1925).

C. G. STORM

Continuous crystallization of green copperas. HARTLAND SEYMOUR. *Ind. Chemist* 1, 307-8(1925).—A continuous process of crystn. is described which is capable of extension to other substances than  $\text{FeSO}_4$ .

E. H.

Hydrogen peroxide, tests and stability. HUGO WASTENSON. *Svensk Farm. Tids.* 29, 317-22(1925).—In prepg.  $\text{H}_2\text{O}_2$  (30%) the water must be free from Fe and Cu. Traces of Pb, Zn, Ba and As have no influence on the keeping property of  $\text{H}_2\text{O}_2$  solns.

A. R. ROSE

The methylene blue test. A contribution to the question of evaluating activated charcoal. W. MECKLENBURG. *Kolloid-Z. Special No.*, Apr. 1, 1925, pp. 132-42; cf. Wiechowski, *C. A.* 9, 2797; Sperry, *C. A.* 17, 2034.—Weighed quantities of C dried at  $120^\circ$  were introduced as quickly as possible into 200-cc. flasks contg. 20 cc. of a 0.15%  $\text{H}_2\text{O}$  soln. of methylene blue. The flasks were shaken only until a good suspension of the C was obtained. The time between the beginning of the shaking and the disappearance of the blue color was measured. The relation between the time  $Z$  required by the active C to decolorize the  $\text{H}_2\text{O}$  soln. of methylene blue and the quantity  $m$  of the C used is expressed by  $(m - a)Z = K$ , in which  $a$  is the quantity of C just sufficient to decolorize the soln. in infinite time and  $K$  is a time const. The relation between  $a$  and  $K$  and the sp. external surface was detd. as follows: wood charred at  $500$ - $600^\circ$  with  $\text{ZnCl}_2$  was finely powdered and sepd. into 8 fractions by sifting through a current of air. Examin. with a microscope and ocular micrometer showed the particles of each fraction to be approx. the same size and form. By considering the surface and weight of the particles proportional, resp., to the sq. and the cube of the dimensions, it was found that the relative sp. surface  $O$  of the different fractions varied between 1 and 0.8. With increasing  $O$ ,  $a$  gradually decreased. The relation between  $K$  and  $O$  was  $KO^{0.5} = k$ . The value of  $k$  varied between  $9.9 \times 10^3$  and  $14.7 \times 10^3$  with an av.  $11.6 \times 10^3$ .

H. M. McLAUGHLIN

BRAIDY, HENRI: La fabrication de l'acide sulfurique par le procede de contact. Paris: Editions de l'Industrie chimique (H. Mounier). 298 pp. Paper covers, Fr. 15. Reviewed in *Chem. Trade J.* 77, 40(1925).

Sulfuric acid. W. A. S. CALDER and CHANCE & HUNT, LTD. *Brit.* 228,646, Nov. 10, 1923. In processes as described in *Brit.* 126,320 (*C. A.* 13, 2258) and *Brit.* 206,229 (*C. A.* 18, 1181) for condensing fumes evolved during concn. of  $\text{H}_2\text{SO}_4$ , steam is introduced through an ejector into the gases in a pipe to give them necessary moisture and velocity before their passage through constrictions for condensation.

Sulfuric acid. C. R. DOWNS. U. S. 1,547,167, July 28. Boiling S is used to regulate the temp. of the reaction in oxidation of  $\text{SO}_2$  with catalysts. The S may be placed around the tubes contg. the catalyst.

Catalysts for making sulfur trioxide. P. AUDIANNE and G. BACHALARD. *Brit.* 228,633, Nov. 8, 1923. See U. S. pat. 1,518,043 (*C. A.* 19, 382).

Concentrating nitric acid. F. C. ZEISBERG. U. S. 1,546,910, July 21. Waste acid contg.  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  is denitrated or dil.  $\text{HNO}_3$  is concd. by passing downward through a heated tower. Before the acid is introduced into the tower, it is heated to above  $30^\circ$  but below its b. p.

Phosphoric acid and phosphorus. H. A. BRASSERT, W. H. WAGGAMAN and H. W. EASTERWOOD. *Brit.* 228,185, Jan. 23, 1924. In reduction of phosphates to produce  $\text{H}_3\text{PO}_4$  or P, an app. is used comprising furnace, flues, downcomer, dustcatcher and regenerator, each of which is provided with ports and valves for regulated admission of air or oxidizing gases when it is desired to effect oxidation of the P formed.

Hydrocyanic acid. J A DU BOIS Brit. 228,303, June 29, 1923  $\text{NH}_4\text{CNS}$  soln. is admitted drop by drop into a vessel heated to about  $350^\circ$  and air, which may be preheated, is introduced. The gases produced are led through a quartz tube contg. pieces of quartz and heated to  $500^\circ$ . Other thiocyanogen compds. (which if not volatile may be atomized from soln with superheated steam) may be similarly employed for producing  $\text{HCN}$ , at  $350$ – $750^\circ$ , with clay,  $\text{SiO}_2$ , Fe, Al, etc., as catalysts.

Zinc oxide. W T GIDDEY, W. G. RAGO and CHANCE and HUNT, LTD Brit. 228,214, Oct. 29, 1923 Crude Zn oxide or carbonate is dissolved with  $\text{NH}_3$  or  $\text{NH}_4$  carbonate, insol. matter is sepd., and the soln. is purified by blowing air through it to remove Mn, adding an alkali carbonate or alkali if necessary to combine with any sulfate present and removing other metals such as Pb, Cu, Cd and Co by  $\text{NH}_4$  sulfide or Zn. A salt of Pb or Cu (if not already present) is added to activate the Zn. The purified soln. is dild. and then distd.

Arsenates of alkaline earth metals. J. ALTWEGG U. S. 1,545,873, July 14 Ca arsenite or other alkaline earth arsenite is heated in a continuous current of O.

Alkali metal cyanide. C. B. JACOBS U. S. 1,546,932, July 21. Material contg. both alkali metal cyanide and carbonate is leached with  $\text{H}_2\text{O}$  at a temp. of about  $36$ – $40^\circ$ , to dissolve both cyanide and carbonate, until a soln. substantially satd. with cyanide is obtained. This soln. is cooled to a temp. between  $10^\circ$  and  $0^\circ$  and the cyanide crystals formed are sepd.

Soluble phosphates. J. G. WILLIAMS and J. T. MILLAR. Brit. 228,220, Sept. 28, 1923 Pptd. di-Ca phosphate is treated with  $\text{H}_2\text{SO}_4$  or  $\text{H}_3\text{PO}_4$  and an alkali or  $\text{NH}_3$  sulfate or bisulfate to obtain alkali or  $\text{NH}_3$  phosphate. Similar use of other Ca phosphates is also referred to.

Aluminum chloride. C. W. HUMPHREY U. S. 1,546,290, July 14 An Al sulfate is treated with NaCl or other alkali metal chloride and  $\text{H}_2\text{O}$  and heated to form  $\text{Al}_2\text{O}_3$  and HCl and the  $\text{Al}_2\text{O}_3$  is then chlorinated.

Aluminum chloride. H. I. LEA and C. W. HUMPHREY. U. S. 1,546,289, July 14 Al sulfate is dehydrated and then chlorinated to form anhydrous  $\text{AlCl}_3$ .

Treating glauconite. PERMUTIT COMPANY. Brit. 228,380, March 17, 1924 Glauconite is first washed alternately with  $\text{H}_2\text{O}$  and with a NaCl soln. (which may be made slightly alk. with NaOH) and is then treated with a soln. of Na silicate and with a dil. soln. of acid reaction, preferably one contg. Al sulfate. This may be followed by a further treatment with NaCl soln.

Coating sodium perborate or other finely divided substances. A. WELTER. U. S. 1,546,156, July 14 Finely divided materials such as Na perborate are permitted to fall through a reaction chamber in which they are sprayed with fine particles of Na silicate or other coating material in liquid form and the liquid coating on the particles is subjected to the evaporative effect of an air current.

Hypochlorite composition. MATHIESON ALKALI WORKS, INC. Brit. 228,588, Oct. 1, 1923. A compn. which is stated to be stable and adapted for use in prepg. solns. of definite strength contg.  $\text{NaOCl}$ , on addition to  $\text{H}_2\text{O}$ , comprises a dry mixt. of stable  $\text{Ca}(\text{ClO})_2$ , (which may be prepd. as described in Brit. 195,366, C. A. 17, 3576) contg. free alkali, and  $\text{Na}_2\text{CO}_3$ .

Grading tungstates or other crystalline substances for use in radioelectric screens, etc. P. L. G. MARCOTTE U. S. 1,546,499, July 21.

Colloidal sulfur. H. VOGEL. U. S. 1,546,048, July 14 In producing highly dispersed colloidal S solns.,  $\text{SO}_2$  and an excess of  $\text{H}_2\text{S}$  are simultaneously introduced into  $\text{H}_2\text{O}$  in a reaction vessel. Cf. C. A. 18, 1885.

"Carbon dioxide snow." T. B. SLATE. U. S. 1,546,681, July 21. Liquid  $\text{CO}_2$  under pressure is conducted into a chamber where the pressure is reduced and from which free gas is withdrawn, so that a portion of the  $\text{CO}_2$  is converted into "snow." U. S. 1,546,682 relates to an app. for producing " $\text{CO}_2$  snow."

Catalysts comprising metal and silica gel. L. H. REYERSON. U. S. 1,547,236, July 28 Adsorbed gases are removed from silica gel by the action of a vacuum and replaced by H while the temp. is lowered to  $-15^\circ$  to  $-30^\circ$  to facilitate adsorption of the H upon the surfaces of the material. The latter is then treated with a soln. of a metal salt such as a salt of Cu, Ag or Pt for sufficient time to permit reduction of the metal by the adsorbed H so that all the surfaces of the porous carrier are coated with a metal film of ultramicroscopic proportions. Catalysts thus formed may be used for hydrogenating oils or for  $\text{NH}_3$  synthesis.

Apparatus for reactivating catalyzers. J. P. HARRIS U. S. 1,546,381, July 21. Catalyzers such as those formed of Ni, which may have been used for hydrogenating oils,

are treated with H at about 220° in admixture with oil and fresh catalyst, in a pipe coil connected with the hydrogenating tank.

**Active carbon.** NAAMLOOZE VENNOOTSCHAP ALGEMEENE NORIT MAATSCHAPPIJ. Brit. 228,582, Aug 9, 1923 Raw or predistd material such as fruit pits, wood, peat or lignite, in finely divided condition, is fed into a hot chamber where it is maintained in suspension in gas; the activated portion is finally drawn off by reason of its lower apparent sp. gr.

**Decolorizing carbon.** E. HEINE U. S. 1,547,037, July 21. Porous mineral coal is mixed with  $K_2SO_4$  or other alkali metal compd. reducible to sulfide on heating with carbonaceous material, the mixt. is heated to at least 600° and alkali metal compds. are subsequently dissolved out from the C produced.

**Artificial pearls and mother of pearl.** J. PAISSEAU U. S. 1,546,309, July 14. In the manuf. of artificial pearls and mother of pearl, Ba hyposulfite is incorporated in a plastic material such as a gelatin or nitrocellulose compn.

**Refractory wicks.** C. BUBERL U. S. 1,546,616, July 21. Si carbide mixed with a binder such as feldspar or enamel and borax is used for making wicks which are adapted for use in oil burners. Flour,  $H_2O$  and linseed oil also may be added.

**Asbestos friction composition.** E. BUISSON U. S. 1,547,408, July 28. Asbestos fibers are electroplated with metal, e. g., Cu, in order to render them coherent so that the material can be formed into solid blocks adapted for use in clutches or brakes.

**Stencil sheets.** A. WAELE Brit. 228,247, Oct 29, 1923 Various colloidal coating mixts. adapted for use on Yoshino paper are described which may comprise gelatinous substances, oil and bentonite. Brit. 228,248 relates to generally similar compns. Cf. C. A. 19, 1619

**Removing coloring substances from organic plastic materials.** J. M. WEISS. U. S. 1,547,187, July 28. Organic coloring matter is removed from dyed celluloid, softened with  $EtOAc$ , or other organic plastic materials by the addition of a peroxide of an org. acid, e. g., phthalyl peroxide.

**Composition for removing carbon deposits from internal-combustion engines.** S. C. DENNIS. U. S. 1,546,479, July 21.  $PhNO_2$ , furfural and  $BuOH$  or other aliphatic alc.

**Polish for automobiles, furniture, etc.** E. N. WYLLIE U. S. 1,545,870, July 14. Powdered whiting 1 qt. is mixed with  $H_2O$  1 qt. while cold, turpentine  $\frac{1}{2}$  oz. is mixed with paraffin base lubricating oil 2 qts. while cold, and the latter mixt. is then added to the first mixt. with violent agitation "in a vertical plane only" until emulsification is effected.

## 19—GLASS, CLAY PRODUCTS, REFRACTORIES AND ENAMELED METALS

G. E. BARTON, C. H. KERR

The modern production of sheet glass. W. E. S. TURNER. *J. Roy. Soc. Arts* 73, 821-37(1925). E. H.

The properties of clays. A. V. BLEININGER. *2nd Colloid Symposium Monograph* 1925, pp. 80-98.—The properties of clays are considered under the following heads: aggregate structure, mineral composition and micro-structure, fineness of grain, chem. compn., clay suspensions, plastic state, dry state, effect of heat, fired state, testing.

JEROME ALEXANDER

Results of an X-ray investigation of the crystalline nature of china clays, etc. G. SHEARER. *Trans. Ceram. Soc. (England)* 23, 314-7(1924).—Spectrographs of powd. samples of clays heated to 1200° and 1700° were very similar to those of natural sillimanite. When clay is heated with  $Al_2O_3$  (1-2) a new cryst. phase appears and very little if any free  $Al_2O_3$  and sillimanite are found.

H. F. KRIEGE

The action of heat on kaolinite and other clays. I. J. W. MELLOR AND A. SCOTT. *Trans. Ceram. Soc. (England)* 23, 322-9(1924).—The dehydration of kaolinite does not take place at a fixed temp.; it is completed above 500°. At this temp. kaolinite decomposes into free  $SiO_2$ , free  $Al_2O_3$  and  $H_2O$ . The exothermic break in the heating curve about 900° is connected with a transformation in the form of the  $Al_2O_3$ . Sillimanite similar to the natural mineral can develop below 1200° and probably above that temp. forms solid solns. with  $3Al_2O_3 \cdot 2SiO_2$ . Above 1700°  $3Al_2O_3 \cdot 2SiO_2$  may be formed.

H. F. KRIEGE

The behavior of clays, bauxites, etc., on heating. III. H. S. HOULDSWORTH

AND J. W. COBB. *Trans. Ceram. Soc. (England)* 23, 279-92 (1924); cf. C. A. 18, 1372.—The change responsible for the exothermic effects observed at 950° with clays could be completed on continued heating at 900° and that occurring with  $\text{Al}_2\text{O}_3$  at 1060° could be completed at 1000°. These changes in clays and in pure  $\text{Al}_2\text{O}_3$  are distinct and different phenomena. None of the indications of exothermic and endothermic reactions with clays can be attributed to the presence of small amts. of impurities and their possible interaction with the clay. No evolution of heat at 950° was found when mixts. of  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  (previously heated to 700° and 400° resp.); of the compn.  $\text{Al}_2\text{O}_3 + 2\text{SiO}_2$  were heated, or when mixts. of the compn.  $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 + \text{SiO}_2$  prep'd. from sillimanite, cyanite, andalusite or allophane, and  $\text{SiO}_2$  were heated. H. F. KARRON

Chemical constitution of brick clay. A. DEMOLON. *Compt. rend.* 180, 1518-20 (1925).—Quartz and combined  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , free and combined  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{K}_2\text{O}$ , combined  $\text{H}_2\text{O}$ , and  $p_{\text{H}}$  are tabulated for the clay and the 5 fractions into which it was sepd. by levigation. The results indicate an isomorphous mixt. of aluminosilicates. Identification of glauconite in the sand fractions indicates it as the source of the ferri-silicates, of the  $\text{K}_2\text{O}$  other than that from mica, and of the free  $\text{Fe}_2\text{O}_3$ . The deposit contains no appreciable amt. of S compds., though the tertiary deposits from which it originates contain numerous pyritic elements. There is 0.4-0.7% total  $\text{P}_2\text{O}_5$  and no free  $\text{Al}_2\text{O}_3$ . A. PAPINEAU-COUTURE

Electrical porcelain; the effect of varying the composition of some of its properties. ERNEST WATKIN. *Trans. Ceram. Soc. (England)* 23, 185-210 (1924).—With the use of cup-shaped test pieces for sp. resistance and dielec. strength detns. and the usual methods for mech. strength, porosity and d. detns., W. found that (a) Substituting feldspar for flint reduces the maturing temp., increases vitrification, sp. gr. and dielec. strength while mech. strength and sp. elec. resistance are decreased. (b) Clay in place of flint increases dielec. strength and sp. resistance but lowers the mech. strength. (c) Substituting ball clay or red clay for china clay has a deleterious action on all properties investigated. (d) Substituting Zr silicate for flint greatly increases the mech. strength, with little effect on the elec. properties. (e) Steatite in place of feldspar greatly increases the sp. resistance, with no other effects. H. F. KARRON

Spark plug. M. WATAYA. *Report Osaka Ind. Research Lab. (Japan)* 5, No. 8, 1-30 (1924).—German spark plug porcelain (Robert Bosch make) was chemically and microscopically analyzed. W. then prep'd. various porcelain bodies using 5 different sources, and compared them with others. The ratio in all mixts. was  $\text{MgO}:\text{Al}_2\text{O}_3:\text{SiO}_2 = 12.33:0.95:19.58$ . The ingredients used were (a) talc, (b)  $\text{SiO}_2$ , (c) Korean kaolin, (d) Japanese clay, and (e) a Manchurian rock (the last contg. 16% loss on ignition, 44  $\text{SiO}_2$ , 0.57  $\text{Al}_2\text{O}_3$ , 0.91  $\text{Fe}_2\text{O}_3$ , 0.25 C, 47.82  $\text{MgO}$ ). Conclusions: The main constituent of the porcelain of Bosch spark plug must be talc. If the porcelain is made of talc, with limestone as a fluxing agent, the product is not good from every point of view. The porcelain contg. the Manchurian rock as a body possesses the highest insulating power at a high temp. but its resistance to quick temp. change is greatly lowered. The porcelain contg. 80 parts talc and 0-15 clay is the best and kaolin is much better than plastic clay. The product thus prep'd. is superior to the Bosch in insulating power, resistance to extreme changes of temp. as well as to higher voltages. Full data are given. S. TASHIRO

Influence of the glaze upon the physical properties of porcelain. E. GEROLD. *Keram. Rundschau* 33, 188-90 (1925).—Different glazes had a marked influence upon the following properties of high-tension porcelain insulators: (1) modulus of elasticity, (2) tensile strength, (3) modulus of rupture, and (4) resistance to impact. The same glazes tested on different bodies influenced the properties of these bodies in the same way. The glazes not only changed the properties of thin bodies but also had a marked influence upon the thicker bodies. The influence of 3 glazes upon the properties of a porcelain was studied. All 3 glazes increased the elasticity coeff. Two glazes decreased and one increased the tensile strength. Two glazes decreased and one increased the modulus of rupture. Two glazes decreased the resistance of the porcelain to impact while one had little influence. The modulus of rupture and the resistance of the body to impact became practically the same as those of the unglazed body after the glazes had been ground off. The elasticity coeff. was somewhat higher on the body from which the glaze had been ground off than that of the unglazed body. As the glaze was slowly ground off the tensile strength approached that of the unglazed body. As the outer skin of the body was ground off the strength of the porcelain decreased markedly, showing that the outer skin imparts strength to the porcelain. The influence of these glazes upon the properties of insulators 72 mm. thick was almost as great as that upon bodies 20 mm. thick. H. G. SCHUECHT

Use and manufacture of silica bricks. R. JORDAN. *Chaleur et industrie* 6, 135-9 (1925).—A discussion of the qualities required and of the defects which must be avoided, with a detailed description of the method of manuf. by which these results are obtained.

A. PAPINEAU-COUTURE

Action of blast furnace and open-hearth slags on firebrick and on silica and magnesite bricks. J. PRELLER AND V. KORBER. *Chem. Listy* 18, 383-9 (1924).—The corrosion of refractory bricks in the lining of an iron blast furnace or open-hearth reverberatory is increased by a rise in the proportions of free ferrous and manganous oxides in the slag, by a decrease in the viscosity of the slag, and by an increase in the amt. of free  $\text{SiO}_2$  in the bricks. The severity of the corrosion is inversely proportional to the d. of the bricks and to the proportion of sillimanite formed in the parts of the lining in contact with the slag.

B. C. A.

Corrosion of firebricks, silica bricks and magnesite bricks by blast-furnace and open-hearth furnace slags. J. PRELLER AND V. KORBER. *Chem. Listy* 19, 9-15 (1925); cf. preceding abstr.—Basic open-hearth slags exert a very corrosive action on  $\text{SiO}_2$  bricks. This may be reduced by decreasing the amt. of  $\text{FeO}$  in the slag and increasing the  $\text{CaO}$  content so as to reduce its mobility and also by ensuring the max. conversion of quartz to tridymite and the highest d. possible in the bricks used in the lining. Care should be taken to avoid conditions favorable to the conversion of the quartz or tridymite into cristobalite.

B. C. A.

The influence of phosphoric acid and phosphates on the rate of inversion of quartz in silica-brick manufacture. W. HUGILL AND W. J. REES. *Trans. Ceram. Soc. (England)* 23, 304-6 (1924).—No effect on the rate of inversion of quartz with phosphate addns. could be found by sp. gr. detns.

H. F. KRIEGER

New use for sillimanite. W. J. REES. *J. Soc. Chem. Ind.* 44, 359 (1925).—Sillimanite may be used for making semi-permanent molds for repeated castings in iron, steel and other metals. The high refractoriness of sillimanite and its small drying and firing shrinkage when bonded with 15 or 20% fireclay render it particularly suitable.

H. H. S.

The porcelain enameling of iron castings. WM. THOMASON. *Ind. Chemist* 1, 273-8 (1925).—A review.

E. H.

The behavior of metal oxides in ground coats on sheet metal. L. VIELHABER. *Keram. Rundschau* 33, 53-5 (1925).

H. G. SCHURECHT

Solubility of glazes and enamels used in cooking. G. W. MONTER-WILLIAMS. *Analyst* 50, 133-4 (1925).—Some cheap enameled ware (mostly from France) was found to contain Pb, which was dissolved appreciably by dil. citric acid solns. In several cases some enameled hollow ware was attacked by dil. citric acid and considerable  $\text{B}_2\text{O}_3$ , as well as Al and Fe was dissolved from the glaze.

W. T. HALL

The microscopic relations of sulfides and silica in blast-furnace and converter linings (PHEMISTER) 8.

Furnace, etc., for glass manufacture. P. KUCERA. U. S. 1,546,544, July 21.

Crown glass. R. J. MONTGOMERY. U. S. 1,545,508, July 14. Sb oxide 1-20% (usually about 2-3%) is used in crown glass in order to prevent undue discoloration by the action of sunlight.

Cerium glass composition. R. J. MONTGOMERY and M. R. SCOTT. U. S. 1,545,509, July 14. About 16% of Sb oxide is used in Ce glass compos. in order to cut off ultra-violet rays.

Fused silica. L. B. MILLER. *Brit.* 228,191, Jan 25, 1924. See U. S. pat. 1,537,036 (C. A. 19, 1935).

Shaping fused silica. E. THOMSON and H. L. WATSON. U. S. 1,546,266, July 14. A mold is filled with particles of substantially pure cryst.  $\text{SiO}_2$  and the mass is heated throughout to a temp. sufficiently high to convert the  $\text{SiO}_2$  into the vitreous state, causing expansion and coalescence and shrinkage counteracting the expansion.

Firing ceramic ware. F. W. HIGGINS. U. S. 1,546,382, July 21. Special supporting plates with legs or spacers are used, formed of bonded  $\text{SiC}$  or other material which has a higher modulus of rupture at  $1350^\circ$  than 300 lbs. per sq. in.

Tunnel kilns for salt glazing of pottery, etc. A. M. DUCKHAM and WOODALL-DUCKHAM (1920), LTD. *Brit.* 228,230, Oct. 20, 1923.

Pottery. W. VERSHOVEN. *Brit.* 228,233, Oct. 24, 1923. Molded ceramic articles which are to be first air-dried and then baked at temps. under  $1000^\circ$  are formed by the addition of  $\text{CaCO}_3$ , a fluoride, and  $\text{SiO}_2$  to clay; e. g., a mixt. may be formed

comprising  $\text{Al}_2\text{O}_3$  30,  $\text{NaF}$  5,  $\text{SiO}_2$  60 and  $\text{CaCO}_3$  5 parts. A larger proportion of fluoride produces a non-separable glazed surface and addition of Ca salts causes the product to bake white and free from Fe spots.

**Refractory material.** C. F. GESSER. U. S. 1,546,833, July 21. Refractory articles such as bricks or furnace linings are formed of  $\text{SiC}$ ,  $\text{Al}_2\text{O}_3$  and a binder produced by the reaction of  $\text{SiC}$  on  $\text{Al}_2\text{O}_3$  at a high temp.

**Porous refractory material.** M. L. HARTMAN. U. S. 1,545,539, July 14. Refractory articles such as heat-insulating bricks are formed with previously burned porous crystal aggregates, e. g., an aq. mixt. of kaolin clay,  $\text{SiC}$  grains and wood flour.

**Silicon carbide abrasive.** M. F. BESCHER, A. A. KLEIN and W. W. GREENWOOD. U. S. 1,546,115, July 14.  $\text{SiC}$  grains are bonded with a coating and uniting compn. of protective ceramic material capable of being fused to a glassy condition at Seger cone 10. The materials are fired together at a temp. which will fuse the bonding material without dissociating the  $\text{SiC}$ .

**Abrasive cement.** H. O. KEAY. Brit. 228,415, June 2, 1924. See Can. 245,795 (C. A. 19, 713).

## 20—CEMENT AND OTHER BUILDING MATERIALS

J. C. WYTT

**Autogenous healing of concrete.** D. A. ABRAMS. *Concrete* 27, 50(1925).—Concrete specimens loaded to failure at 28 days but not shattered were exposed to weather and again tested at the age of 5 yrs. The av. compressive strength of five cylinders was: 28 days, 2380 lb.; 8 years, 5100 lb. per sq. in. RAYMOND WILSON

**Cement and concrete.** ANON. Kansas City Testing Lab., *Bull.* 18, 3-14(July, 1925).—A booklet contg. information on cement and concrete including specifications, tables, etc. J. C. WYTT

**Expanded concrete.** K. P. BILNER. *Concrete & Constr. Eng.* 20, 325(1925).—Concrete weighing as little as 30 lb. per cu. ft. may be made by mixing with the concrete a finely powdered metal which reacts with  $\text{Ca(OH)}_2$  soln. to form hydrogen. The hardened product has much better heat insulating properties than brick or ordinary concrete. RAYMOND WILSON

**Requirements of cement for modern highway construction.** A. T. GOLDBECK. *Proc. Am. Soc. Testing Materials* (preprint) No. 33(June, 1925).—The influences which produce tensile stresses in concrete pavements are shrinkage due to drying, contraction due to decrease of temp., warping due to variations in temp. and moisture, bending due to heavy wheel loads applied frequently, bending due to non-uniform subgrade support, excessive compressive stress due to rise in temp. or increase in moisture content or both, and frost action. Concrete for highway construction would be even more suitable from a technical standpoint than at present if it developed high tensile strength within a very few days, had a very low shrinkage factor under the action of moisture and temp. and had a greater resistance to alternations of freezing and thawing, wetting and drying, changes in temp. and repeated loads. J. C. WYTT

**Analytical properties of set and hardened mortars.** E. E. BUTTERFIELD. *Proc. Am. Soc. Testing Materials* (preprint) No. 40, 1-9(June, 1925).—The cement content may be calcd. from the detn. of  $\text{CaO}$  in mortars proportioned by the method of mortar voids or with inupdated sand with an av. variation of 1%. In other samples the variation between cement used and cement found was 15%. J. C. WYTT

**Modern methods for the conservation of wooden poles.** E. M. SHAPOSHNIKOV. *Elektrichestvo*. 1925, 372-5—A review. C. G. F.

**A theory on the mechanism of the protection of wood by preservatives.** V. Further work on hydrocarbons. ERNEST BAYEMAN and CARLETON HENNINGSEN. *Proc. Am. Wood Preservers' Assoc.* 1924, 33-7; cf. C. A. 14, 1063; 16, 628, 4041; 18, 2064.—Soly. and toxicity detns. of the following 12 hydrocarbons from the aromatic, naphthene and paraffin series are given: benzene, toluene, mesitylene, durene, naphthalene, diphenyl, acenaphthene, cyclohexene, cyclohexane, dihydronaphthalene, tetrahydronaphthalene, tetrahydroacenaphthene, normal hexane, octane and hexadecane. Hexane was found to be 10 times as toxic as benzene but is too volatile to be of value. The other members of the paraffin series are too insol. to be toxic. The naphthenes are sol. and toxic to a greater extent but do not compare with the aromatic hydrocarbons. Efforts to increase the soly. and toxicity of paraffin hydrocarbons by the addition of other compds. were unsuccessful. ALFRED L. KAMMERER

**A new and rational process of wood preservation.** E. R. BESENFELDER. *Chem.*

**Zig. 49, 525-6(1925)**—Green wood is rapidly dried, sterilized, and conditioned by exposure to the vapor of a water-absorbing org. liquid such as benzene in a closed vessel provided with a condenser for solvent recovery and sepn. of water therefrom. After removal of water, the system is closed. The condensation of the vapor causes a reduced pressure, which, in turn, accelerates the vaporization of the solvent from hot wood. A suitable preservative dissolved in the same solvent used for the water removal is introduced without breaking the partial vacuum. A rapid and complete impregnation takes place, because of the suction created by the condensation of the vapor in the pores of the wood. When the impregnation is complete, the vessel is drained. The solvent still in the wood is recovered by a reversal of the above process, i. e., steam is passed through the system. Besides preservative material such as carbolineum, water-repellent and finishing substances such as rosin, montan wax, stearin, and palmitin can be used.

ALFRED L. KAMMERER

**Relation of temperature and pressure to the absorption and penetration of zinc chloride solution into wood.** J. D. MACLEAN *Proc. Am. Wood Preservers' Assoc.* 1924, 44-73.—As a result of expts. at the Forest Products Laboratory and at the treating plant of the Union Pacific Ry. it is shown that high soln. temps. are very effective in improving the absorption and penetration of  $ZnCl_2$ . If the temp.-pressure combination is too high collapse of the wood fiber will result. The following combinations may be taken as safe limits, 140 to 150 lbs. at 200°, 175 lbs. at 175° and 170 lbs. at 185°.

ALFRED L. KAMMERER

**Temperature changes in wood under treatment.** R. M. WIRKA, *Proc. Am. Wood Preservers' Assoc.* 1924, 285-93.—Yellow-pine piling Sections 9 to 17 inches in diam. and 40 inches long were subjected to steam and vacuum treatments in an especially designed cylinder at the Forest Products Lab. to study the effect on the internal temp. of the wood, of variable steam periods and steam pressures and vacuum periods.

ALFRED L. KAMMERER

**The comparative resistance of seventeen species of wood-destroying fungi to sodium fluoride.** C. A. RICHARDS, *Proc. Am. Wood Preservers' Assoc.* 1924, 37-44.—Seventeen of the common wood-destroying fungi were tested on malt bacto-agar in Petri dishes. *Leptia trabea* was the most resistant and *Poria incrassata* the least resistant to NaF, the former fungus requiring a 0.3% concn. and the latter a 0.1% concn. to kill.

ALFRED L. KAMMERER

**Visual determination of penetration of sodium fluoride in treated wood.** G. T. PARKER and H. A. GRAUQUE, *Proc. Am. Wood Preservers' Assoc.* 1924, 20-2.—The wood section is sprayed with 5% soln. of  $K_2Fe(CN)_6$ , dried and followed by 5%  $FeNH_4$  chloride. When color develops the surface of the wood is washed under the tap. The untreated portion is colored a deep blue. The treated portion remains unchanged.

ALFRED L. KAMMERER

**Report of Committee 4-3, Preservatives.** ERNEST BATEMAN, *et al.*, *Proc. Am. Wood Preservers' Assoc.* 1924, 73-86.—The Committee presents for adoption as standard, specifications for the following: creosote, grades 2 and 3 for ties and structural timbers; high-boiling or anthracene oil for brush or spray treatment including method for distn.; water-gas-tar distillate and soln. for use with  $ZnCl_2$ . Data on low-temp. tars are presented, including a list of chief American manufacturers, estd. production for 1924 and analyses of typical tars. A revision of the standard float test of the residue in creosote is proposed, prescribing more sharply defined limits.

A. L. K.

**Report of Committee 4-7. The use of petroleum with creosote and other toxics.** R. S. BELCHER, *et al.*, *Proc. Am. Wood Preservers' Assoc.* 1924, 117-78.—Many data are presented including toxicity tests, methods of analysis, physical and chem. characteristics of various mixts., studies of the mixt. of petroleum with low-temp. tars and with  $ZnCl_2$ . Detailed reports of track inspections of mixt.-treated ties on the Santa Fe and Southern Pacific are given. Among the Committee's conclusions are the following: the petroleum used should be preferably of asphalt base, should not yield more than 1.5% sediment on mixing with creosote, should have a min. flash point in a closed tester of 225° F. and its viscosity should be sufficiently low to permit proper penetration of the mixt.; petroleum increases the mechanical life of the wood by retarding checking; mixts. contg. sufficient creosote to prevent decay are economical; results from  $ZnCl_2$ -petroleum ties indicate that the addition of petroleum adds to the service obtainable. No recommendations are made as to the percentages of creosote and petroleum in mixts. nor as to retention per cu. ft.

ALFRED L. KAMMERER

**Report of Committee 5. Treatment.** J. R. HELSON, *et al.*, *Proc. Am. Wood Preservers' Assoc.* 1924, 191-246.—Specifications for the treatment of ties, timber, piling, poles and posts with oil, salt solns. and combinations thereof by full and empty

cell pressure processes and non-pressure processes are presented; also recommendations as to the quantity of preservative to be injected per cu ft for each process and each class of timber.

ALFRED L. KAMMERER

Report of Committee 7-1. Track service records. Z. M. BRIGGS, *et al.* *Proc. Am. Wood Preservers' Assoc.* 1924, 246-52.—A table is prescribed showing the ties per mile used in renewals by 15 railroads, 1900 to 1922. Additional completed service tests of 9 woods in the Forest Products Lab records are included, also progress reports of special test tracks on the B. & O., C. B. & Q., C. M. & St. P. and the W. P. railroads.

ALFRED L. KAMMERER

Report of Committee 8. Steam treatments. G. M. HUNT, *et al.* *Proc. Am. Wood Preservers' Assoc.* 1924, 265-84.—Expts. at the plant of the International Creosoting & Construction Co., Texarkana, Tex., steaming 18 ft yellow-pine piles (av diam 6 in.) for various periods and at various pressures showed the following results: with green material at 20 lbs. steam pressure followed by 2 hrs. vacuum a max. moisture reduction (8.2%) was reached after 6 hrs., while higher pressures for the same period gave a slightly greater reduction (9.8%); seasoned material showed a gain under the same treatment; temp. readings taken at different depths showed a temp. gradient decreasing from the center to the outside. A test at the U. P. Plant, Laramie, Wyo. on hewn lodge pole pine ties showed that steam treatment increases the water content in dry ties and causes only a slight decrease in wet or green ties. A test at the Forest Products Lab. on green red-oak specimens 4' x 4' x 4', 6' x 6' x 4' and 6' x 10' x 4', with steam at 20 lbs. from 2 to 6 hrs. followed by vacuum, showed that there was a large gain in water on steaming but a rapid loss on applying vacuum with a considerable resulting net loss, although the material was not seasoned, the dryest piece contg. 45% water. The wood was badly checked.

ALFRED L. KAMMERER

Report of Committee No. 17, Wood Preservation, Appendix B. Service test records. R. H. HOWARD, *et al.* *Proc. Am. Ry. Eng. Assoc.* 1924, 853-60.—A study of service records to date indicates the following comparative value of tie treatment, due consideration being given to the kind of wood, climate and physical condition of track: zinc chloride 6 to 15 yrs., zinc creosote 8 to 18 yrs., empty-cell creosote 17 to 25 yrs., full-cell creosote not warranted on account of decay protection exceeding mechanical life. A table is included showing tie renewals per mile (1900 to 1922) on various railroads using treated ties extensively.

ALFRED L. KAMMERER

Report of Committee No. 17, Wood Preservation, Appendix E. Creosote mixture with petroleum. HERMANN VON SCHRENK, *et al.* *Proc. Am. Ry. Eng. Assoc.* 1924, 862-95.—Reference is made to mixt. treatments of ties on the Hungarian and Austrian State Railways, also to expts. in India. Results of detailed inspection of exptl. ties treated in 1908 and 1909 by the A. T. & S. F. Ry. are given. The Committee makes no definite recommendation.

ALFRED L. KAMMERER

Report of Committee No. 17, Wood Preservation, Appendix F. Zinc-petroleum mixture for treatment of ties. HERMANN VON SCHRENK, *et al.* *Proc. Am. Ry. Eng. Assoc.* 1924, 895-7.—The Committee inspected zinc-petroleum ties treated by the A. T. & S. F. Ry. in 1902, 1915 and 1917 and by the Southern Pacific Ry. in 1914. The 1902 ties gave an av. life of 11.7 yrs. The 1914, 1915 and 1917 ties are still in good condition. The addition of the petroleum reduces the tendency of zinc chloride treated with ZnCl<sub>2</sub> to check and split.

ALFRED L. KAMMERER

White hydraulic cement. I. J. COX. U. S. 1,547,365, July 28. A mix of Fe-free limestone and Fe-free labradorite is sintered and ground.

Concrete walls or blocks. N. C. JOHNSON. Brit. 228,538, Feb. 2, 1924. A colloidal paste which may contain tannic acid, starch and H<sub>2</sub>O and which prevents the setting of the cement at the surface is applied to the surface of blocks or walls of concrete in order to insure exposure of the aggregate at the surface of the finished product. Sugar and CaCl<sub>2</sub> also may be used in mixts. for this purpose.

Bituminous concrete mixtures. PORTOR SOC. ANON. AND M. LEVY. Brit. 228,257, Aug. 3, 1923.

## 21—FUELS, GAS, TAR AND COKE

A. C. FIELDNER

The nature and utilization of coals. HANS TROPSCH. Z. Ver. deut. Ing. 69, 890-901 (1925).—Largely a discussion of the "oil and solid bitumen" content of various coals (as detd. by extr. with C<sub>6</sub>H<sub>6</sub> at 270° and sepn. of the 2 kinds of bitumen by pe-

roleum ether) and its relation to the coking properties; cf. Fischer C. A. 19, 2402. The relative ease of hydrogenation of various coals by  $H_2$ ,  $HCO_2Na$ , or by the Bergius process is also reviewed. The information thus attainable as to the relative chem. compn. of coals is applicable to the detn. of their proper utilization. WM. B. PLUMMER

Pressure and the elucidation of the chemical constitution of coal. R. QUARENDON. *Chemistry and Industry* 44, 676-9 (1925).—A résumé of the results reported upon studies of the effect of pressure on the chem. constitution of coal, with a bibliography of 31 references. While the high temp. which obtains in most high-pressure studies doubtless has a large effect in bringing about the observed changes, by causing an increase in the reaction velocity, nevertheless it is conceivable that the pressure also plays an important role by forcing the reaction upon the coal substance. The reluctance in ordinary circumstances of complex substances like coal to undergo transformations which one might expect them to undergo, attributable to the great size of the mol., has largely a physical rather than a chemical basis, and may be considered a phenomenon comparable with those rationally embraced by the term "steric hindrance." W. C. EBAUGH

Cleaning tests of Central Illinois coal. THOMAS FRASER AND H. F. YANCEY. *Bur. Mines, Tech. Paper No. 361*, 23 pp. (1925). E. H.

The artificial drying of peat. GAETANO CASTELLI. *Rass. min. met. chim.* 62, 56-60 (1925).—A description, with quant. data of recent developments. C. C. D.

The ash content of solid fuels. J. FOLLMANN. *Brennstoff-Chem.* 6, 205-8 (1925).—By treatment with  $HCl$  and  $HF$  solid fuels can be practically completely sepd. into mineral and org. constituents. The wt. of mineral matter is sometimes more than (brown coal, lignite), and sometimes less than (bituminous coal) that of the ash as detd. by combustion. J. D. DAVIS

Synthetic petroleum. LUIGI DAL PRATO. *Rass. min. met. chim.* 62, 64-7, 91-3, 113-6 (1925); cf. C. A. 19, 1492.—A description of processes for synthesizing hydrocarbon fuels from C, H and from simple gaseous compds. of these elements, including the industrial prepn. of illuminating gas, water-gas,  $CH_4$ , and  $H_2$ , the polymerization of  $CH_4$ ,  $C_2H_4$  and  $C_3H_6$ , the hydrogenation of  $C_2H_2$  and C (Sabatier, Berthelot, Fischer and Bergius) and their transformation to liquid hydrocarbons, the oxidation of C and of  $CH_4$  to liquid fuels by the Fischer process and the synthesis of petroleum by the Olivier and Burgeols process. C. C. DAVIS

The gas tester of Dr. Ott. FRIEDRICH LUX. *Gas u. Wasserfach.* 68, 448-9 (1925).—The app. consists of a modified form of the ordinary lab. Bunsen burner, the primary air inlet being graduated and accurately controllable. The amt. of air necessary to cause the burner to begin to "pop" is taken as an index of the gas quality, it depending mainly on the B. t. u. but also on the d. and the compn. WM. B. PLUMMER

Oxygen in gas. J. F. WING. *Proc. Am. Gas Assoc.* 1924, 1345-6.—It has not been possible to det. accurately the decrease in the O content of city gas between the holder and distant points in the system, but tests indicate an 0.05% decrease through 18 miles of mains. No greater accuracy can be hoped for as the O content at the holder inlet may vary 0.15% hourly and since the error in the Hempel analysis using either P or pyrogallol is 0.05-0.10%, and therefore no definite conclusions can be drawn from the data as to the action of O in the mains or meters. WM. B. PLUMMER

The modern aspects of coal carbonization in Germany. CANTIENY, Z. *Ver. deut. Ing.* 69, 547-53, 929-32 (1925).—The operating and economic advantages of externally heated rotary retorts are pointed out, and the KSG (Kohlenscheidungs-Gesellschaft) retort installation at the Mathias Stinnes mine (Karnap) is described in detail. It consists of two concentric, slightly inclined shells. The coal is fed into the lower end of the inner shell, carried through it by a helical screw fixed to its inner wall, the coal being thus preheated to 200°; at the top of the retort it drops into the outer carbonizing shell. The outer shell is externally heated by gas, the temp. of the combustion gases being reduced to 700° by recirculation of flue gas from the cold end of the retort chamber, so that the max. temp. of carbonization is 500-30°. The flow of coke through the carbonizing shell is by gravity, the gas being removed at the upper end. Outside dimensions of the retort are approx. 3 m. diameter and 23 m. long, the total time the coal is in the inner and outer shells being 2.5 hrs. when the time of rotation is 90 sec. The coal has 3.0%  $H_2O$ , 25.0% volatile matter, 14.8% ash, and is fed in the powdered form with admixture of 10% of fines from the semi-coke produced. As it is a strongly caking and swelling coal the through-put is 60-80 tons/24 hrs., but with non-caking coals this can be considerably increased. With 5% steam through the carbonizing shell the yields are 82% semi-coke, 5.05% primary tar, 0.48% thick tar, 0.43% light oil, and 69 cu. m. gas/ton. The semi-coke is denser than that from most retorts the % of fines (under 10 mm.) being 42% for ordinary quenching and 30% if inert-gas cool-

ing is used. If pulverent semi-coke may be used as powdered fuel, for briquetting, as an addn. agent to improve the coke from poorly coking coals, and for smelting Sn or Zn ores if it is fairly well caked and lumpy it is useful for industrial or domestic heating for gasification, or in foundry cupolas. A "M A N" gas producer 3.0 m. diameter has operated satisfactorily on a semi-coke contg. 17% H<sub>2</sub>O, 18.2% ash, and 10.6% volatile, whose screen analysis was 33% 0-5 mm., 9% 5-10 mm., 26.5% 10-20 mm., 31.5% 20-90 mm., the heating value of the gas made being 1300 kg. cal./m. In foundry practice it has been found possible to reduce the fuel from 24.5 kg. coke/300 kg. Fe to (7 kg. coke + 11 kg. semi-coke)/300 kg. Fe, saving approx. 25% on the fuel and hence decreasing the S taken up by the Fe despite the increased S content of the semi-coke; it has not, however, been possible to use straight semi-coke. A general discussion follows, various situations being pointed out in which the low-temp. carbonization of coals is justified. WM. B. PLUMMER

**Economics of coal carbonization in rotary retorts.** E. ROSSER. *Brennstoff-Chem.* 6, 153-8 (1925).—That low-temp. carbonization is economically feasible is shown by figures for yields from a 90-ton Thyssen oven working on various coals together with tables based on current prices for products and raw materials in the Ruhr. Advantages of the rotary retort or oven over other carbonizing app. are: (1) Simple construction, (2) simple operation, (3) low installation and operating costs, (4) high thermal efficiency (90%). J. D. DAVIS

**The wash-oil problem.** H. KEIMSTEDT. *Brennstoff-Chem.* 6, 185-8, 201-5 (1925).—Reasons for thickening of tar oils, almost universally used in Germany for scrubbing light oils from gases, are discussed at length. A number of factors are probably operative in thickening, "the thickening process depends primarily on the properties of the wash oil used but the rapidity at which it progresses is strongly influenced by the working method and the compn. of the gases washed." H<sub>2</sub>S, NH<sub>3</sub>, CN and moisture in the gas probably promote the thickening since these tend to attack iron containers and the dissolved iron effects polymerization catalytically. Oxygen exerts a strong polymerizing influence; it was shown in the lab. that fresh wash oil could be completely converted into soft pitch by passing through it 400 times its vol. of O. When the wash-oil was sepd. into phenols and neutral oils it was found that the former was converted into soft pitch by 200 vols. of O, whereas the viscosity of the latter increased only slightly. Used wash-oil was polymerized more quickly, doubtless as a result of impurities contd. therein. J. D. DAVIS

#### Manufacture and properties of absolute alcohol (LORSETTE) 16.

LISTER, J. E. and HARRIS, C. H.: *The Theory and Practice of Combustion.* London: E. Benn, Ltd. 150 pp. 6s.

**Solid oil fuel.** R. ILLEMAN. U. S. 1,546,785, July 21. See Brit. 206,889 (*C. A.* 18, 1191).

**Solid fuel containing alcohol.** H. S. MORK and G. J. ESSELEN, JR. U. S. 1,545,595, July 14. A solid infusible fuel comprises alc., the reaction product of a fatty acid and a caustic alkali, e. g., of stearic acid and NaOH, and a considerable proportion of "methyl acetone" or other liquid which is a non-solvent of the reaction product.

**Fuel briquets.** P. W. KUNZE. U. S. 1,547,252, July 28. A binder for making combustible briquets is prepd. by adding lime to acid resin, heating to 200-250° for several hrs. and treating the mass with air during this time.

**Dewatering peat.** O. SÖDERLUND, T. BOBERG, N. TESTRUP and TECHNOCHEMICAL LABORATORIES, LTD. Brit. 228,628, Nov. 7, 1923. A large quantity of H<sub>2</sub>O is first added to wet peat to facilitate primary sepn. of the peat fibers and associated colloids without the application of pressure, and the fiber is subsequently pressed and is dried by waste gases. An app. is described.

**Apparatus for making illuminating gas from air and hydrocarbons.** J. T. GRAHAM. U. S. 1,545,755, July 14.

**Gas producer of the downward combustion type.** H. GOENTZ. U. S. 1,547,213, July 28.

**Gas generator.** F. UMFLEBY. Brit. 228,280, Nov. 16, 1923. Pulverized fuel and air, O, CO<sub>2</sub> or steam are fed to the interior of a cylindrical furnace or generator with or without CaCO<sub>3</sub> or CaO. Catalysts such as Al, Ce, Co, Cu, Ir, Fe, Ni or Pt may be used in the furnace lining.

**Gas-purifying apparatus.** J. A. SHAW. U. S. 1,545,703, July 14. The app. is

adapted for purifying coke-oven gas, etc., by treatment with  $\text{Na}_2\text{CO}_3$  soln and regeneration of the latter

**Carbonizing solid fuel.** J RUDR Brit 228,763, May 23, 1924 Solid fuel is carbonized consecutively in internally and externally heated retorts. The gases produced in the externally heated retort are mixed with the gases for internal heating. An app is described

**Carbonizing coal.** J ROBERTS Brit 228,686, Jan 2, 1924 A mixt. of a caking coal with a non-caking coal contg 20–45% volatile matter as specified in Brit 187,336 is heated to  $760\text{--}850^\circ\text{C}$ , a caking coal contg 7.5% of substances sol in pyridine and  $\text{CHCl}_3$  is mixed with an equal quantity of a non caking coal contg 6.5% of similar substances and the mixt crushed to a 10 mesh size Coke breeze may be substituted for an equal amt of non caking coal

**Low-temperature coal distillation.** G CANTIENV U S 1,547,027, July 21. In order to prevent caking of bituminous coal or similar materials, the mass is agitated in the presence of coke during the distn

**Rotary retort for distilling solid carbonaceous materials.** C. A. GRIFFITHS. Brit. 228,740, April 15, 1924 The app is adapted for recovery of oils, pitch and  $\text{NH}_3$ .

**Rotary cylindrical retort for distillation of slate, asphalt, lignite, peat or other bituminous materials.** S KACSER U S 1,547,331, July 28

**Apparatus for the distillation of oil, tar or other liquid carbonaceous materials.** J. B KIRK U S 1,546,285, July 14

**Coking coal.** F SCIDENSCHNUR Brit 228,494, Jan 30, 1924 Coal descending continuously through a shaft is heated by a counter-current of a non oxidizing gas, of which at least 5–6 cu. m. is used for each kg of coal A tar is obtained which is stiff at ordinary temp and a coke which is rich in readily inflammable gases.

**Coke.** W. E TRENT U S 1,545,620, July 14 Pulverized coal is mixed with  $\text{H}_2\text{O}$ , pulverized lime or limestone is mixed with a liquid oil such as gas oil or crude mineral oil, and an amalgamated mass is formed from the 2 mixts which is then coked.

## 22—PETROLEUM, LUBRICANTS, ASPHALT AND WOOD PRODUCTS

F. M. ROGERS

**Investigation of toxic gases from Mexican and other high-sulfur petroleum and products.** Introduction. R R SAYERS, N A C SMITH AND A. C FIELDNER. *Bur. Mines Bull.* No. 231, 1–8(1925).—Outline of the scope of the work and findings. **Production, marketing and refining of light Mexican crude oil.** W A. JACOBS. *Ibid* 9–16.—Outline of the methods of treatment and equipment used Chemical and physical characteristics of typical high-sulfur crudes marketed in the United States. N. A. C. SMITH AND D D STARK *Ibid* 17–36—A no of typical analyses are given. Analysis of the products of lab distns showed that the S concns mainly in the gases and in the residuums, and that distillates of similar b p, even though they are of somewhat different derivation, contain practically the same % of S. A large proportion of the total S in the crude is combined in the form of a black, brittle asphalt, which is insol in  $\text{Me}_2\text{CO}$  but sol. in  $\text{C}_6\text{H}_6$ . Even if this asphalt is entirely removed, about 70% of oil remains, which must be classed as high-S crude. Composition and amount of toxic gases given off in the handling and refining of light Mexican crude oil. G W. JONES AND W. P. YANT. *Ibid* 37–48— $\text{H}_2\text{S}$  is the highly poisonous constituent in the gases found in the production, transportation and refining of high-S crude oil. Hydrocarbon vapors also are injurious. In general, concn of  $\text{H}_2\text{S}$  in the gases decreases in the following order from crude stills, pressure stills, and containers for crude oil. Containers for finished products showed no  $\text{H}_2\text{S}$  Evolution of  $\text{H}_2\text{S}$  in exceedingly large amounts is almost continuous throughout a run of Mexican crudes. Industrial methods for eliminating toxic gases from high-sulfur Mexican petroleum. W. A. JACOBS AND C. W. MITCHELL. *Ibid* 49–57—Brief description of precautions used in various parts of the plants, with general recommendations for minimizing the gas hazard. Correlation of the data obtained from refinery accidents with a laboratory study of hydrogen sulfide and its treatment. C. W. MITCHELL AND W. P. YANT. *Ibid* 59–80—A discussion of the medical findings in accidents observed in refineries, the toxicity of  $\text{H}_2\text{S}$  as studied by its action on canary birds, white rats, guinea pigs, dogs and goats, and the treatment of  $\text{H}_2\text{S}$ -poisoning bringing out more particularly the advisability of the use of O in cases of acute poisoning. Respiratory protection

from petroleum gases and vapors. S H KATZ AND J J BLOOMFIELD *Ibid* 81-102.— See C. A. 19, 892. A. PAPINEAU-COUTURE

Laboratory shale tests. EROR HOLMBERG *Teknisk Tids* 55, (Kemi afl. 7) 50-4 (1925).—The work on shale under the direction of the "Engineer's scientific academy" is outlined. There is a bibliography of 30 Swedish titles. A R. ROSE

The tar number and the evaluation of transformer and turbine oils. HANS STRÖGER *Z. angew. Chem.* 38, 476-81 (1925).—The usual physical and chem tests are not satisfactory with these oils because of the special qualities required of them, including the ability to withstand oxidation in the air at an elevated temp. Mineral oils, because of their complex and unhomogeneous structure, and also dependent upon the reaction temp and degree of refining, yield as products of oxidation, water, high mol acids, so called asphaltic acids, polymerization products and as intermediates, alcohol, aldehyde- and ketone-like substances. The sum of the decomposition products is transformer-oil sludge, contg. not only the oil-sol. products but also acids and unsatd. compds. The asphaltic acids are assumed to be hydroxy carboxylic acids. The unsatd. compds. may be further self-oxidized and consequently the stability test is entirely unreliable. The acids formed with and without a catalyzer are similar, except those formed under the catalytic influence of lead, which are essentially different. Acid formation precedes formation of a sludge by a definite time and may extend over 1000 hrs., not as a continuous process but in intermittent steps. The "tar number" was added by Kissling to the ordinary unsatisfactory methods for testing turbine oils (cf. *Chem.-Ztg* 30, 432 (1906)). The evaluation of oils in this way is one-sided, since only their acid reaction products are considered and acid and sludge formation are not parallel processes. Moreover in the majority of cases, the sludge is not decidedly acid but is neutral in character, contg. about 50-60% of saponifiable constituents. Two oils having identical tar numbers yielded, upon heating in the air under the same conditions, 2.7 and 0.14% of sludge, resp., with corresponding acid numbers of 0.92 and 0.10. With an increased degree of refinement the tar number of all mineral oils falls and then rises again. The dip is due to a destructive oxidation or cracking process, followed by the release of a large proportion of low-mol., volatile products. The naphthene group of oils is much less susceptible to this action than the metthane group. HARRIET W. GIBSON

The heat of wetting metals with oil and its relation to lubrication. W. BACHMANN AND C. BRÜGGER *Kolloid-Z., Special No.*, Apr. 1, 1925, pp. 142-54.—The substances investigated included (1) oils known to be excellent lubricants; (2) oils of low lubricating power; (3) petroleum with and without the addn. of oleic acid in the sense of Southcombe and Wells (cf. C. A. 14, 1778). The metal used was Cu powder prep'd by reducing with H at 300° the purest Cu(OH), which had been ppt'd in the usual way, very carefully washed and dried at low temp. in a vacuum. For each expt. 20 g. of the Cu powder was introduced into 200 cc. of the oil while the oil was slowly stirred in a Dewar flask. Before introduction of the powder, the oil and the powder in the special app. for its introduction were brought to const. temp. in the Dewar flask. The small heat effect was measured very carefully. The resistance thermometer used consisted of a spool made of 5 glass rods and 2 glass rings around which was wound 0.1 mm. Fe. wire having 100 ohms resistance. The resistance thermometer was calibrated in C.M. against a Beckmann thermometer. The current was measured by a mirror galvanometer and read on a scale on which 1 m. represented 1° temp. difference. The measurements showed that a real (not definitely defined from present data) relation exists between the heat of wetting metals with oil and the lubricating power. Poor lubricating oils had a much smaller heat of wetting than oils known to be good lubricants. A small addn. of an unsatd. acid (oleic) to petroleum produced a relatively large rise of the heat of wetting. This corresponds to the observation of Southcombe and Wells that such addn. favors an increase in the capillary activity of the oil and the formation of stable films with greater capacity for adhering to the surface layer of the metal. The arrangement of the app. is well shown by photographs and figures. H. M. McLAUGHLIN

Measuring the consistency of lubricating greases. W. NORMANN. *Chem. Umschau* 32, 115-7 (1925).—A brass rod 200 mm. long, 9 mm. in diam., and weighing 50 g., with a coniform point at the lower end, is allowed to drop 800 mm. into the sample, in a 14-cm. can of 16-cm. diam.; the no. of mm. which the rod sinks into the grease is the measure of its consistency; the temp. of the sample is carefully taken at different parts of the can and is corrected for 20°. The app. is easily duplicated and is well suited for factory control. P. E. CHER

KLAR, M. *The Technology of Wood Distillation*. Translated by A. Rule. London: Chapman & Hall, Ltd. 496 pp. 25s. net. Reviewed in *Ind. Chemist* 1, 309 (1925).

Oil from oil sands. P. ARBON. U. S. 1,547,197, July 28. Oil sands are subjected to a vacuum within a casing to cause seepage of the oil, which is then elevated through a tubing within the casing by use of pressure free from the influence of the vacuum.

Apparatus for separating oil and gas. E. A. WHITTEN. U. S. 1,547,090, July 21. Retort for distillation of oil from shale, etc. G. McD. JOHNS. U. S. 1,547,396, July 28.

Retort for shale distillation. E. W. HARTMAN. U. S. 1,546,659, July 21. Cracking low-grade petroleum oils. L. S. ARBOY. U. S. 1,547,191, July 28. Crude oil, tarry residue or other low grade petroleum oil is sprayed into a hot current of producer gas at a cracking temp., the product is cooled, condensate is sep'd. and residual gases and vapors are scrubbed with oil of high h. p.

Apparatus for producing gasoline by cracking heavier hydrocarbon oils under pressure. C. ELLIS. U. S. 1,545,949, July 14. The app. comprises heating pipes with a drum of larger diam. above the pipes.

Apparatus for cracking hydrocarbons. S. J. M. AULD, A. E. DUNSTAN and P. H. HERRING. Brit. 228,661, Nov. 29, 1923. The app. is adapted for carrying out the process of cracking specified in Brit. 220,664 (C. A. 19, 725).

Heat-treatment of mineral oils or other liquids. W. G. LAIRD. U. S. 1,546,345, July 14. A liquid such as oil is mixed with a gas, e. g., casing-head gas, and the mixt. is passed to a zone of the max. temp. used. Vapors withdrawn from this zone are passed counter-current to the mixt. in heat interchange relation to form a zone of lower temp. than the first through which the mixt. passes, thereby to obtain a condensate from part of the vapors which is mingled with the mixt. in the second zone.

Apparatus for "converting" petroleum oils. C. P. DUBAS. U. S. 1,546,634, July 21.

Apparatus for heating hydrocarbon oils to effect fractional distillation. W. E. WILSON and H. W. WILSON. U. S. 1,546,035, July 14. The app. comprises a series of compartments communicating near their bottoms through openings in the dividing walls. Each of the compartments has a vapor outlet and oil maintained at a const. level is successively heated to higher temps. in the different compartments.

Lubricant. R. E. WILSON. U. S. 1,547,141, July 21. A lubricant adapted for cold weather use in automotive engines of the type in which liquid fuel enters the oil from the cylinders is prep'd. with a flash point above 65°, a Saybolt viscosity of at least 140 at 38°, a low loss of viscosity during use, and a content of 7-15% of fractions b. 150-240°.

## 23—CELLULOSE AND PAPER

CARLETON E. CURRAN

The gliding plane of cellulose fibers. H. AMERONX. *Kolloid-Z.*, Special No., Apr. 1, 1925, pp. 119-31.—Principally a theoretical discussion of the structure of cellulose fibers based on the conception of Nageli's cryst. micelle. The "displacement lines" which frequently occur in bast-cell membranes appear as if the membrane were decomposed in a det'd. line of fracture into individual pieces shoved obliquely against each other so that the angle of incidence with the longer axis is nearly const. The fibers of bast cells of Urticaceae in their optical behavior are to be compared not with a one-axis crystal but with a crystal aggregate built up out of particles having 2 axes. Other cellulose fibers, such as in the outer covering of many seeds, do not form cylinders but consist of symmetrical, massive striae which may show displacement lines in the most beautiful formations. The geometrical difficulties due to hollow cylinders disappear and this arrangement in its mol. structure more nearly resembles the uniform crystal although they are to be considered crystal aggregates. No displacement lines are formed in artificial-silk fibers. On account of the method of prep'n. and their uniformly anisotropic properties, there seems no doubt that in the artificial fibers long rows of micelle are arranged in parallel. The forces exerted during the growth of the living fibers evidently produce an entirely different regularity in the micelle structure and result in the formation of layers arranged in det'd. directions. This arrangement of the micelle with the phenomena of gliding planes produces a far-reaching similarity between cellulose fibers and true crystals.

H. M. McLAUGHLIN

Wood pulp. G. A. RICHTER. U. S. 1,545,522, July 14. Raw cellulosic material such as spruce chips is digested in an acid cooking liquor contg.  $\text{Na}_2\text{SO}_3$  or  $\text{Na}_2\text{SO}_4$ . The spent acid liquor is sepd., neutralized and concd. and the Na values are recovered by smelting and treating with  $\text{H}_2\text{O}$ . The resulting alk. liquor is carbonated to form  $\text{Na}_2\text{CO}_3$  and the pulp from the first digestion is further digested in the alk. liquor formed. The spent alk. liquor is acidified with  $\text{SO}_2$  to produce an acid cooking liquor for repetition of the first digestion.

Deinking paper, etc. R. W. G. STUYZKE. U. S. 1,545,707, July 14. Material to be deinked is agitated in a soln. of Na silicate and  $\text{NaHCO}_3$  and then washed.

Carbon paper. W. P. PEMBROKE. U. S. 1,546,747, July 21. A slightly saturable carrier sheet is coated with a heated wax-contg. color coating of penetrating qualities, cooled, reheated and again cooled to effect further penetration of the coating.

Carbon for fuel or adsorbent purposes. C. G. SCHWALBE. Brit. 228,512, Jan. 30, 1924. Waste sulfite cellulose lye is carbonized in the presence of a substance "having a large surface development" such as adsorption C, clay or kieselguhr, to which a small amt. of acid may be added, e. g.,  $\text{HCl}$ .  $\text{MeOH}$  may be recovered as a by-product.

Thermo-couple apparatus for determining the moisture content of paper and textile materials. A. R. HARVEY. Brit. 228,477, Sept. 22, 1924.

Treating cellulose with sulfuric and acetic acids. C. DREYFUS. U. S. 1,546,211, July 14. Cellulosic material, e. g., a cotton fabric or filter paper, is treated (at a temp. not substantially above room temp.) with a mixt. of concd.  $\text{H}_2\text{SO}_4$  and  $\text{HOAc}$  contg. not more than 15%  $\text{H}_2\text{O}$ , in order to give a special finish.

Cellulose acetate. V. B. SEASE. U. S. 1,546,679, July 21. High-grade tissue paper or other cellulose fiber is treated with  $\text{HOAc}$ ,  $\text{Ac}_2\text{O}$  and a small % of  $\text{H}_2\text{O}$  based on the wt. of the cellulose, thus introducing at least a substantial part of the  $\text{HOAc}$  and  $\text{Ac}_2\text{O}$  required for acetylation. The material is then treated with a bath contg. any additional  $\text{HOAc}$  and  $\text{Ac}_2\text{O}$  required for acetylation and also contg.  $\text{H}_2\text{SO}_4$  or other acetylation catalyst,  $\text{H}_2\text{O}$  and more  $\text{H}_2\text{SO}_4$  or other inorg. acid are added and the temp. is maintained at 40–65° until a product of desired soly. is formed. It is then pptd. and washed.

Acetylcellulose compositions for coating and impregnating. FARBENFABRIKEN VON F. BAYER & Co. Brit. 228,518, Jan. 29, 1924. Acetylcellulose contg. more than 50%  $\text{HOAc}$  is dissolved in a chlorohydrin or dichlorohydrin and  $\text{H}_2\text{O}$ , with or without pigments, softening agents and other auxiliary ingredients.

Acetic acid recovery from cellulose acetate solutions. J. M. KESSLER. U. S. 1,546,902, July 21. A cellulose acetate soln. contg.  $\text{HOAc}$  and a catalyst (e. g.,  $\text{H}_2\text{SO}_4$ ) is treated with  $\text{NaOAc}$  to neutralize the catalyst and the resulting mixt. is subjected to film evapn. on a heated surface until at least most of the  $\text{HOAc}$  in the film has evapd. and is recovered.

## 24—EXPLOSIVES AND EXPLOSIONS

CHARLES E. MUNROE

Bibliography of material in English on the subject of powder and explosives to the end of the year 1923. T. L. DAVIS. *Mem. poudres* 21, 396–401 (1924). T. L. D.

The decomposition of trinitrotoluene by the action of sunlight. E. WICHEK AND H. DOMAT. *Z. ges. Schiess-Sprengstoffw.* 20, 69–70 (1923).—Kraus and Turck (C. A. 19, 2747) have not shown satisfactory proof of the presence of trinitrobenzoic and picric acids and of trinitrobenzene in their photoreaction product. Exception is also taken to the inference that the bursting of guns from premature explosions may be due to increased sensitiveness of TNT from the action of light or of metals. Schulz and Ganguly (C. A. 19, 2036) have recently shown that very different products result from the action of light on TNT, and claim that the result of their presence is decreased sensitiveness.

C. G. STORM

Examination of certain samples of old acid. M. MARQUEYROL. *Mem. poudres*. 21, 380–5 (1924).—M. reports analyses of mixed acid which had been used for the nitration of cellulose. A certain quantity of nitrocellulose dissolves in the acid during nitration, and on standing in the soln. changes slowly to a low-nitrated material which is insol. and ppts. out. Old used mixed acid consequently changes with time. The samples which M. has analyzed were in the last period of their transformation and on diln. with water yielded a small quantity of ppt. (degraded nitrocellulose) which showed 36.7 cc.  $\text{NO}$  per g. in the nitrometer (2.3% N). They contained no detectable oxalic acid, and no acid substances other than  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ , and  $\text{N}_2\text{O}_5$ , as indicated by careful detns.

by several different methods. Detns. of total acidity to methyl orange, of total  $\text{NO}_2$  by the nitrometer, and of free  $\text{N}_2\text{O}_4$  by titration with permanganate, give all of the data necessary for the complete calcn. of the acid constituents of old mixed acid.

TENNEY L. DAVIS

The explosion catastrophe at Bodio (Tessin) II. ALFRED SCHAARSCHMIDT. *Z. angew. Chem.* 38, 537-41(1925), cf. *C. A.* 18, 587, 588.—It was assumed that the cause of the explosion was the spontaneous decompn. of addition products of  $\text{N}_2\text{O}_4$  and unsat. benzenes, the so-called nitrosates. Such nitrosates can be kept for months at a time at ordinary temps., but they are very sensitive to heat and inclined to explode violently. Mixts. were carried out with cyclohexene, amylene and cetele. Such an olefin and  $\text{N}_2\text{O}_4$  undergo spontaneous heating, with the formation of  $\text{N}_2$  and a greenish oil contg. crystals; this mixt. decomposes slowly when cool, but rapidly at  $70-80^\circ$ , into  $\text{N}_2$ , a little  $\text{NO}$ , and a yellow oil. This last product, when heated to  $140-150^\circ$ , breaks down with the formation of a large quantity of  $\text{N}$ - and decompn. products. Data showing the course of reactions with 3 samples of cyclohexene, and one each of amylene and cetele, are presented. The explanations for the explosion offered by Berl (cf. *C. A.* 17, 2959; 18, 2120) are opposed.

W. C. HBAUGH

Explosive. K. R. BROWN. U. S. 1,516,117, July 14. A sugar is dissolved in a mixt. of glycerol and diglycerol and the soln. thus formed is nitrated with  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ .

Explosive. K. R. BROWN. U. S. 1,516,367, July 21. Nitroguanidine is used as a sensitizer in various perchlorate explosives.

Apparatus for uniform compression of explosive charges. B. GAOTTA. U. S. 1,516,370, July 21. The app. is adapted for manuf. of detonators.

Explosions by use of light metals. II. STAUDINGER. U. S. 1,517,070, July 21. In producing explosions for blasting, use in bursting projectiles, etc., light metals such as Na and K belonging to the 1st and 2nd groups of the periodic classification and reacting substances such as Cl, S or O compds. are brought into "intensive contact" with each other, e. g., by a strong impact.

## 25—DYES AND TEXTILE CHEMISTRY

L. A. OLNEY

The coordination theory in its application to the study of mordant dyes. G. T. MORGAN AND J. D. MAIN SMITH. *J. Soc. Dyers Colourists* 41, 23A-40(1925).—A lecture and discussion in which Werner's coordination theory is applied to quinonoxime, alizarin, azosulphate, aminohydroxyazo, di-o-hydroxyazo and oxidizable monohydroxyazo dyes.

L. W. RIGGS

Azo dyestuff technology. II. The manufacture of Resorcin Brown. CLEMENT WHITENRAD. *Chem. Trade J.* 77, 92-3(1925); cf. *C. A.* 19, 2748.

R. H.

Union dyeing. II. WILKINSON. *Ind. Chemist* 1, 298-302(1925).

R. H.

The chemical foundation of the artificial-silk industry. EMIL HEUSER. *Seiwé Pappiers-Tid.* 27, 180-8, 215-8(1925).—A review.

R. H.

Resume of recent work done in the chemical department of the Shirley Institute. D. A. CLIBBENS. *J. Soc. Dyers Colourists* 41, 248-9(1925).—The chief objects of this work are (1) the detn. of the nature of the minor constituents of cotton and the extent to which they vary in raw material of different origins; (2) the extent to which these constituents are altered or removed during the bleaching process; and (3) the extent to which the cellulose itself is altered by the chem. agents used in bleaching printing and other technical processes. Some research problems in cotton bleaching and dyeing. *Ibid.* 249.—A lecture and discussion.

L. W. RIGGS

Suffocation of silkworm cocoons by chloropicrin. GUIDO COLOMBO. *Giorn. chim. ind. applicata* 7, 15-7(1921).—Chloropicrin can be easily used for the suffocation of silkworm cocoons, but leaves unsolved the more important question of their rapid drying. For this reason the proposed process cannot be made general. There are other objections, too, the danger of handling the chloropicrin and the darkening of the silk. It is also not applicable to small producers, who already possess small, simple, economical and easily transportable dryers.

ROBERT S. POSNANTIER

The influence of substituents on the color of azo dyes (WANNER) 10. Thermo-couple apparatus for determining the moisture content of paper and textile materials (Brit. pat. 228,477) 23.

Azo dyes. K. TITMSS. U. S. 1,546,328, July 14. Diazotized benzaldehyde-azo- $\alpha$ -naphthalenes are coupled with arylamides of the 3-hydroxy-2-naphthalene-carboxylic acid, to form dyes which generally give black dyeings.

Black vat dye. P. NAWIASKY and E. KRAUCH. U. S. 1,546,859, July 21. A dye producing gray to black shades on cotton after exposure to air is formed by treating nitrated dibenzanthrone with S.

Dye for hair and fur. W. KRICHEVSKY and W. K. NELSON. U. S. 1,545,500, July 14. An aq. soln. is formed of 1,2-naphthalenediamine-4-sulfonic acid, with  $\text{FeSO}_4$ , borax and  $\text{NaHSO}_4$  or equiv. compds.

Dyeing. CHEMISCHE FABRIK GRÜSHEIM-ELEKTRON. Brit. 228,510, Jan. 29, 1924. Combined shades of vat and azo dyes are produced by impregnating vegetable fiber with a mixt. of an aromatic nitrosoamine alkali salt, an alkali salt of an arylide of 3-hydroxy-2-naphthoic acid or a substance contg. a reactive methylene group, and an ethereal salt of the leuco compd. of a vat dye. Numerous examples are given.

Dyeing. CHEMISCHE FABRIK GRÜSHEIM-ELEKTRON. Brit. 228,514, Feb. 1, 1924. In a modification of the process specified in the preceding patent the goods are impregnated or printed with an arylide of 3-hydroxy-2-naphthoic acid or with a diacetylacetyl aromatic diamine or monoacetylacetyl aromatic amine such as those described in Brit. 211,772 and Brit. 211,814, and then developed with a diazo soln. An ethereal salt of a leuco-vat dye is used in one of the baths and the material is given a final treatment with an acid oxidizing agent. Examples are given.

Dyeing wool. J. S. WILSON, J. THOMAS and SCOTTISH DYES, LTD. Brit. 228,634, Nov. 8, 1923. Wool is dyed with aq. solns. of 1-methylaminoanthraquinone (which dyes red) or with other aminoanthraquinones. Alc. or other substance which promotes the soly. of the aminoanthraquinone may also be added.

Dyeing cellulose acetate. G. H. ELLIS. U. S. 1,545,819, July 14. Yarns, threads or other products of cellulose acetate are treated with one of the indophenol dyes, e. g., the reduced compd. of dimethyl-*p*-aminophenyl-1,4-naphthoquinonimide. Cf. C. A. 19, 736.

Dyeing cellulose acetates. R. CLAVEL. U. S. 1,546,969, July 21. In dyeing cellulose acetates with vat dyes such as bromoindigo or pyrogene indigo, the dyeing is effected in a hyposulfite vat kept weakly alk. by  $\text{NH}_3$ , caustic alkali being present only in sufficient quantity to form the leuco compd. A protective colloid such as gelatin, glucose or starch, and at least one  $\text{H}_2\text{O}$ -sol. salt, e. g.,  $\text{CaCl}_2$ ,  $\text{MgCl}_2$  or  $\text{BaCl}_2$ , are also used in the vat.

Dyeing cellulose acetate. FARBWERKE FORM. MEISTER, LUCIUS & BRÜNING. Brit. 228,557, Jan. 29, 1924. Acetate silk is dyed violet to blue shades by monosulfonated 1,4-diaminoanthraquinone or 1,4-aminohydroxyanthraquinone, or an alkyl, aralkyl or aryl deriv., having the sulfo group in 2- or 3-position. Salts, acids or protective colloids may be added to the dye bath.

Treating textile materials with bleaching solutions or other liquids under pressure. T. D. ARNSTON. U. S. 1,545,872, July 14. Mech. features.

Bleaching textile fibers. J. R. MACMILLAN. U. S. 1,547,138, July 21. Jute or other fiber is simultaneously treated with a bleaching liquor such as hypochlorite soln. and with  $\text{Cl}_2$ , washed with an alk. wash e. g.,  $\text{NaOH}$  or lime, and then again treated with bleaching liquor.

Viscose and artificial silk. P. BADER, H. EGGERT and A. WAGNER. Brit. 228,348, Feb. 9, 1924. Viscose solns. adapted for the manuf. of artificial silk are freed from alkali sulfide by the use of  $\text{H}_2\text{O}_2$ , alkali peroxides or persulfates or other "per salts" to oxidize the sulfide to sulfate.

Centrifugal spinning apparatus for making artificial silk from artificial resins, filling materials, etc. O. SINDL. Brit. 228,497, Feb. 2, 1924.

Apparatus for forming threads from viscous material. J. P. HOOPER. U. S. 1,546,133, July 14.

Finishing cotton fabrics. T. B. RUSHTON, E. A. FOURNEAUX and CALICO PRINTERS' ASSOCIATION, LTD. Brit. 228,654, Nov. 17, 1923. In treating cotton fabric as specified in Brit. 196,896 (C. A. 17, 3795), it is given a high permanent luster or linen effect by subjecting it, while the threads are in a somewhat plastic condition, to a calendaring, swissing, schreinerung, glazing, embossing, or similar heat and pressure treatment, so that the moisture in the threads is evaporated and the threads are flattened. The heat and pressure treatment may follow the thiocyanate treatment or may follow an "alter-mercerization" treatment. Brit. 228,655 specifies the treatment of fabrics with alkali for mercerization and with a soln., at a temp. of 80-155°, contg. one or more thiocyanates, which may be mixed with neutral salts, of such a concn. that it ceases

to be a solvent of cellulose. The fabric may be given repeated alternate treatments to produce various decorative effects.

**Pyroxylin-coated fabric.** G. C. BACON U. S. 1,545,935, July 14. Cretonne or other fabric is dyed with a dye of the indanthrene series and then given a thin coating of pyroxylin material.

**Mercerizing, etc., woven fabrics.** R. P. FOULDS and TOOTAL, BROADHURST LEE Co., LTD. Brit. 228,585, Sept. 22, 1923. All (or stenciled portions) of a fabric of cellulosic fiber is treated with  $H_2SO_4$  of "craping" strength without use of  $CH_3O$ , mercerized with or without tension (before or after the  $H_2SO_4$  treatment) and finally embossed or compressed. The first and second steps of the treatment may be carried out on the yarn if desired, before it is woven.

**Softening parchementized fabrics.** R. P. FOULDS and F. L. BARRETT. U. S. 1,546,121, July 14. Cotton fabric is incompletely parchementized with  $H_2SO_4$  of d. somewhat less than 1.55 in the presence of formaldehyde and the fabric is then softened by treatment with  $H_2SO_4$  of less than parchementizing strength.

## 26—PAINTS, VARNISHES AND RESINS

A. H. SABIN

**Anti-corrosive paints.** R. G. DANIELS. *Ind. Chemist* 1, 271-2(1925).—A review E. H.

**Industrial nitrocellulose products—varnishes and enamels.** H. HEPPWORTH. *Ind. Chemist* 1, 290-2(1925).—A review. E. H.

**Analysis of rosin oil.** J. LAGERQUIST. *Stenskt Kem. Tids.* 37, 131-53(1925).—Many numerical data are given. Artificial rosin oil is most often detected by low sp. gr. and n. A. R. ROSE

**What do we know about rosin oil?** J. LAGERQUIST. *Stenskt Kem. Tids.* 37, 89-99(1925).—At the end of this review is a list of 61 org. compds. isolated and identified from pyrogenous products of pine resins. This table includes known phys. consts. There are 44 references in the table and more than 30 in the text. A. R. ROSE

**Transfer ink.** W. S. LAWRENCE. U. S. 1,545,837, July 14. A fusible, adherent transfer ink adapted for making transfers by hot pressing comprises a mixt. of "Cumar" with thickened castor oil and rapeseed oil. Some of the oils form a soln with the "Cumar" and some are present as sepd. small particles.

**Transfer ink for marking leather.** W. S. LAWRENCE and F. W. BARKER, JR. U. S. 1,545,836, July 14. A solid fusible, non-smear transfer ink comprises coloring material in a vehicle formed of shellac 12, rosin 12 and butyl tartrate 2 1/2 parts.

## 27—FATS, FATTY OILS, WAXES AND SOAPS

E. SCHERUBEL

**Rapid procedure for the determination of the iodine-bromine number of fat.** L. W. WINKLER. *Z. Nahr. Genussm.* 49, 277-80(1925); cf. C. A. 19, 1061, 2138.—The absorption of Br by fat is catalyzed by Hg salts while acetates will hasten the reaction by removing the HBr as it is formed, which tends to arrest it. Prep. a soln. contg. 3 cc. Br in 1 l. glacial AcOH; standardize each time it is to be used with 0.1 N  $Na_3AsO_3$  or against pure castor oil, which has a very const. 1 no. (84.3) (0.1269 g. oil requires 8.43 cc. 0.1 N Br.). Weigh out fat, the quantity depending on the 1 no.: 200-0.05 g.; 100-0.1 g.; 50-0.2 g.; 30-0.3 g.; 10-1.0 g. Add 2-3 cc.  $CCl_4$  and dissolve by gentle warming. Add 0.1 g. each of pulverized  $HgCl_2$  and  $NaC_2H_3O_2 \cdot H_2O$ . Titrate with the Br-AcOH soln. to a yellow color which is maintained for 1/4 min. Heat to boiling; if any salt remains undissolved add 2-3 cc.  $H_2O$ ; if the color has disappeared continue to add Br-AcOH until the yellow color persists for 2-3 min. Results of detns. on several samples show good comparisons with methods where Br is added in excess and time permitted for absorption. FRANK E. RICE

**Determination of the iodine number of drying oils.** PAUL GILLOT. *Ann. fals.* 18, 335-41(1925).—In order to obtain accurate results by the Hübl method with oils having a high I no., the oil must remain in contact with the reagent at least 24 hrs., or else 5 cc. of reagent must be used per cc. of oil and allowed to act for 8 hrs. Even under these conditions the detn. can be affected by a large no. of factors which can interfere

with the accuracy of the results. Max I absorption can be obtained via Wijs in 30-60 min with 2-2.5 cc. of reagent per cc. of oil (60% excess of I). It gave very concordant results with oils of *Mercurialis* (C. A. 19, 2139), slightly higher (about 3 units) than the Hubl method. Properly prep'd Wijs' reagent will keep its strength unaltered for over a month, and can still be fit for use after several yrs. A soln. 5 times as strong as Wijs' reagent fell in strength from 13.33 to 12.19% free I in 16 yrs. A. P. C.

Determination of the iodine number of fats. THURE SUNDBERG *Ann. fäls. 18*, 341-2 (1925), cf. C. A. 14, 2557-8—*Controversialis* August (C. A. 7, 280). A. AUGUST, *Ibid.* 342-3—Reply to Sundberg. A. PAPINEAU-COUTURE

Rancidity of olive oil in Egypt. A. AZADIAN *Ann. fäls. 18*, 343-7 (1925)—Periodic analyses of samples of different origins carried out over a period of 1 yr. showed no appreciable increase in acidity during that period, and no direct relationship between the acidity and ultimate rancidity of the oils. Rancidity apparently develops to an equal extent in oils having little or no acidity, and in those having relatively high acidity. The intensity of the reactions used for detecting rancidity (Vintilescu and Popescu, Isoglio, Kreiss, Viedmann) is not proportional to the degree of rancidity, and the value of these reactions is limited by their hypersensitiveness. Oils of all origins became rancid within 1 yr. A. PAPINEAU-COUTURE

The bleaching of animal and vegetable fats and oils. BRUNO HASSEL *Chem.-Ztg.* 49, 546-8 (1925)—This is a discussion of known methods. By using from 1 to 3.5% of a prep'n made by Merck contg. 60% H<sub>2</sub>O<sub>2</sub>, H was able to bleach dark fish, soy and coconut oils, extd. from fuller's earth, at temps. of 55° to 75° in 1½ to 4 hrs. Upon sapon. the bleached fish oil reverted in color and developed its original odor which had been removed. Edible fats bleach readily with this reagent but require a subsequent neutralization to remove the taste of the bleach. E. SCHERUBEL

The unsaponifiable matter of arctic sperm oil. MITSUMARU TSUPIMOTO *Chem. Umschau* 32, 127-8 (1925)—A sample of arctic sperm oil showed the following const.: d<sub>4</sub><sup>20</sup> 0.8752, acid no. 1.8, sapon. no. 114.9, I no. (Wijs) 86.0, n<sub>D</sub><sup>20</sup> 1.4645, R.-M. no. 11; % fatty acids 57.4, % unsapon. matter 43.2, % cholesterol 0.17. Fatty acids: just liquid at 5°, neutralization no. 195.1 no. 91.1, polybromides 5.3%; m. p. of the unsapon. matter 24-25° and I no. 72.0. The unsapon. matter consists of about 70% oleic alc., much cetyl alc. and 0.4% cholesterol. The presence of Scharling's dodecyl alc. could not be confirmed. The Grun-Janko bromine-ester method used in the above work is apparently applicable for the preparative sep'n. of the satd. and unsatd. wax alc. P. ESCHER

The unsaponifiable constituents of shark and ray-liver oils. V. Y. TOYAMA *Chem. Umschau* 32, 113-5 (1925); cf. C. A. 18, 3733—The unsapon. matter of the *Aburatsunozame* liver oil yielded small quantities of an ether-insol. bromide and another bromide insol. in petr. ether. The former was debrominated with Zn and glacial AcOH and the highly unsatd. alc. liberated; its I no. is 282.9; the sapon. no. of its acetylated product is 230.8. Similar ether insol. bromides were obtained in minute quantities from the unsapon. matter of the liver oils of other sharks (*Kagurazame*, *Ondenzame* and *Itachizame* oil) and of the giant torpedo. A genetic relationship seems to exist between batyl, chimyl and selachyl alcs. on the one hand and stearic, palmitic and oleic acids on the other hand; the latter acids correspond with octodecyl, cetyl and oleic alc. P. ESCHER

Suitability of fish oils for the manufacture of olein. C. STEPEL *Chem.-Ztg.* 49, 593-4 (1925)—Low distn. temp. gives high yields, causes little change in the I no. (higher temps. lower the I no.), and changes the character of the distillate but little from that of the crude fatty acids, while higher temps. produce more change. The comp'n. of the pitch in both cases differs from that of other animal fats. There are few hydrocarbons, but saponifiable fats of low acid no., higher sapon. no. and viscosity (polymerized lactonized fatty acids) are present in quantity. By distn. the formation of hydrocarbons is retarded in favor of highly polymerized fatty acids. The lower the yield of pitch the more is the character of the fish oil preserved in the distillate. The fatty acids which incline to the formation of lactones give the fishy character to the oil. The behavior of these during distn. depends on the initial temp. and the rapidity of its rise; and distillates of different character are produced. It is possible to produce distillates free from fishy character. The process is protected by patents; and oils of suitable comp'n. furnish a satisfactory material for the manu. of olein. E. S.

Colloid chemistry and the soap industry. A. IMHAUSEN, *Kolloid-Z., Special No.*, Apr. 1, 1925, pp. 83-6—A review of the work of Zsigmondy (cf. C. A. 18, 3284) and its contribution to the soap industry. H. M. McLAGHLEN

Preserving fats with inert gases. P M HEVERDAHL U S 1,546,237, July 14 See Brit. 207,551 (C A 18, 1552)

Soaps. P. VILLAIN Brit 228 282, Nov 7, 1923 Soaps which remain permanently transparent are prepd by mixing, at a temp of about 50°, a transparent soap, equal weights of "methylated spirit" and a perfume, together with 1-5% of a sol cellulose deriv, such as viscose or cellulose acetate butyrate or acetobutyrate Various medicaments, etc may be added to the soap

Soaps or bleaching compositions containing sodium pentaborate. J S MORGAN and PATENT BORAX CO, LTD Brit 228 459, Aug 20 1924

Saponaceous detergents. R VIDAL Brit 228 390 April 1, 1924 A detergent miscible with H<sub>2</sub>O without sepn of its components is formed from soda castor oil soap 30-35, oleic acid or acids of copra oil 10-15 and 'pale oil' or gas oil 30-35 parts or from other similar ingredients

## 28—SUGAR, STARCH AND GUMS

F W ZERBAN

The new continuous diffusion apparatus of Rak A LINSBAUER Z *Zuckerind cecho-slov Rep* 49, 89-92, 97-9, 106-10(1924) *Listy Cukrovarnické* 42, 477 ff (1923-4) — The disadvantages of the old continuous diffusion systems were low and irregular extrn Rak has designed a new system consisting of 3 open diffusion cells  $D_1, D_2, D_3$ , connected at the bottom to 3 vertical pulp presses  $P_1, P_2, P_3$ . The pulp presses press upward. Around the top of each diffuser is a discharge launder  $L_1, L_2, L_3$ . This is closed on the inside by a screen. Fresh chips enter at the top of  $D_1$ , pass down and into the bottom of  $P_1$ , up through  $P_1$  into the top of  $D_2$ , etc. Press water from  $P_1$  and fresh warm water enter at the bottom of  $D_1$ , juice overflowing from  $L_1$  and press water from  $P_1$  go to the bottom of  $D_2$ , etc., juice being finally withdrawn from  $L_3$ . The diffusers have vertical shafts with spiral arms to agitate the chips and feed them downward toward the intake of the presses. Since the vol. of the chips is reduced by the presses,  $D_1$  and  $P_1$  are installed in duplicate. The av. of 3 tests on a 3-cell battery (as described above) shows: fresh slices, polarizing 10.7%, pulp to  $D_1$  9.13%, to  $D_2$  4.4%, leaving, 1.97%, wt of pressed slices, 46.9% on fresh beets. Juice entering  $D_1$ , 2.12° Bx, 1.42 polarization, 0.70 purity; entering  $D_2$ , 5.32° Bx, 4.26 polarization, 80.1 purity, diffusion juice, 14.87° Bx, 13.4 polarization, 90.2 purity. Water used, 63% on beets, draft, 116%, unknown loss, 0.21% on beets, known loss 0.93%, total 1.14%. Av. of 3 tests on a 4-cell battery (like the above with  $D_3$  and  $P_3$  in duplicate but with  $D_4$  and  $P_4$  added) show: fresh slices, polarizing 10.23%, pulp to  $D_1$  8.03%, to  $D_2$  3.8%, to  $D_3$  1.83%; leaving, 0.98%; wt of pressed pulp leaving, 40.9% on fresh beets. Juice entering  $D_1$ , 1.07° Bx, 0.50 polarization, 46.7 purity; entering  $D_2$ , 2.14° Bx, 1.32 polarization, 61.7 purity; entering  $D_3$ , 3.93° Bx, 2.95 polarization, 75.1 purity; diffusion juice, 14.03° Bx, 12.3 polarization, 87.8 purity. Water used, 67% on beets; draft, 125%; unknown loss, 0.25% on beets; known, 0.40%; total, 0.65%. The advantages of the system are no waste water, much smaller water consumption, small wt of pulp, small space and first cost, simple control, little labor (1 man), low losses

W. L. BADGER

Coloration of juices in different systems of evaporation. A LINSBAUER AND J. FISER. Z. *Zuckerind. cecho-slov. Rep* 49, 25-9, 33-8, 41-7, 49-54, 57-63, 65-70(1924); *Listy Cukrovarnické* 42, 337 ff (1923-4) — Tests of 2.5 days each were made on 6 evaporator installations, full data being given for each. Test A, sample quintuple; Robert bodies, heating surfaces (a) and boiling points (b). — I (a) 265 sq. m. (b) 109°; II (a) 290, (b) 101°; III (a) 320, (b) 93°, IV (a) 355, (b) 83°, V (a) 390, (b) 57°. Color per 100 polarization referred to thin juice as 100, 100° 1.13 1.21 1.43: 1.55 1.84. Test B, combination quintuple; Wellner-Jehne bodies, I (a) 864 + 610, (b) 109°; II (a) 400, (b) 97°; III (a) 396, (b) 90°, IV (a) 450, (b) 82°, V (a) 500, (b) 65°. Color 100: 1.26 1.43: 1.55 1.70: 1.85. Test C, combination quadruple, I (a) 550 vertical + 360 horizontal, (b) 104°; II (a) 550 vertical + 360 horizontal, (b) 99°; III (a) 265 horizontal, (b) 89°; IV (a) 265 horizontal, (b) 83°. Circulators on 1st effect, 60 sq m. Color, 100: 1.07: 1.33: 1.46: 1.50. Test D, combination quadruple; I (a) 307 vertical + 335 horizontal, (b) 112°, II (a) 350 + 161 horizontal, (b) 106°, III (a) 122 vertical + 182 horizontal, (b) 85°; IV (a) 175 + 100 vertical, (b) 57°. Circulators on 1st effect, 120 sq. m. Color, 100: 1.40 1.99 2.26 1.91. Test E, combination quadruple with pre-evaporator; pre-evaporator, (a) 145, Kestner, (b) 124°; 1 (a) 375, Kestner, (b) 111°; II (a) 520 horizontal, (b) 102°; III (a) 252 horizontal, (b) 82°, IV (a) 350 horizontal,

(b) 63° Color 100 117 153 138 140 157 Test F, pressure triple with after-concentrator first 3 bodies Viucik-Turek, concentrator Robert, 1 (a) 750, (b) 117°, 11 a) 750 (b) 112° III (a) 750, (b) 105°, concentrator (a) 180, (b) 95°. Color, 1.00.-1.21 1.32 1.44 1.59 Where heating surfaces are too large, circulation is poor, or working irregular the increase of color is greater. Horizontal bodies give better circulation on thick juice, vertical on thin juice. Test A shows a large increase of color in the last effects and small increase in first (all vertical) while test B (all horizontals) shows the reverse. The Kestner (test E) at 124° does not show serious increase in color; the large increase in color in 1 of test E is due to storage of hot juice between the pre evaporator and I for a relatively long time. The pressure evaporator shows very small increase in color the increase in the concentrator being due to filtration and storage of hot thick juice after III before the concentrator. The larger the no of units of which the evaporator is composed, the greater the increase in color. A good review of the literature is included.

W. L. BADGER

A brief account of the refining of sugar. C. M. KEYWORTH. *Chemistry & Industry* 44, 723-5(1925)

E. H.

### The solubility of sucrose (MONDAIN-MONVAL) 2.

Refining sugar solutions. C. STEFFEN. Brit 228,741, April 1, 1924. In a process for the pptn. of Ca trisaccharate from sugar solns by use of powdered lime, the lime is strewn on a liquid surface as free from scum as possible. An app. is described.

## 29—LEATHER AND GLUE

ALLEN ROGERS

Alfred Seymour-Jones. R. W. GRIFFITH. *J. Am. Leather Chem. Assoc.* 20, 358-60(1925)—An obituary.

J. A. WILSON

The dual nature of chrome tanning—a preliminary note. K. H. GUSTAVSON. *J. Am. Leather Chem. Assoc.* 20, 382-9(1925); cf. C. A. 19, 1961.—Certain negatively charged Cr complexes have tanning properties under certain conditions. The addn of  $\text{Na}_2\text{SO}_4$  to Cr liquors causes some of the Cr ions to enter negative complexes and to give a fuller leather in tanning, which is characteristic of the tannage with these complexes.

J. A. WILSON

Significance of the results which have been obtained on (leather) belting research. JABLONSKI. *Ledertech Rundschau* 16, 177-82(1924)—A review. The value of research is pointed out.

I. D. CLARKE

Synthetic tannins as auxiliary tannins and their use in sole and heavy leather in general. VITTORIO CASABURI. *Ledertech Rundschau* 17, 41-5, 57-62(1925)—Several English and Continental methods of tanning with syntans are outlined.

I. D. CLARKE

The influence of different methods of sulfiting on the salting-out of quebracho extract and a simple method for determining the salting-out value of tanning extracts. R. LAUFFMANN. *Ledertech Rundschau* 17, 89-90(1925)—To det. the "salting-out value" of a tanning ext. shake 100-cc portions of the filtered ext. soln, contg. 1 g. tannin, with 11, 22 and 32 g. resp. of  $\text{NaCl}$  for 2 hrs., filter through paper and det. tannin in the filtrate by Lowenthal's method. Treatment of quebracho ext. with  $\text{NaHSO}_4$ ,  $\text{Na}_2\text{SiO}_3$  or  $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$  caused a decrease in the amt. salted out, a decrease in the size of the colloidal particles and a decrease in tanning action.  $\text{Na}_2\text{SO}_3$  was least effective.

I. D. CLARKE

The extraction of tanning materials in the tannery. LEOPOLD POLLAK. *Gerber* 51, 105-7(1925)—A discussion of factors effecting the yield.

H. B. MERRILL

New tanning materials and tannery sundries. LEOPOLD POLLAK. *Gerber* 51, 116-7(1925)—Analytical data for 2 soaps and 1 ext.

H. B. MERRILL

Report of the work of the German research laboratory for the leather industry at Freiberg during the year 1923. PÄSSLER. *Ledertech Rundschau* 16, 17-20, 30-2, 33-4(1925), cf. C. A. 19, 1506.—A report of analytical work.

I. D. CLARKE

Hide and leather imperfections caused by follicular mange. R. W. FREY. *J. Am. Leather Chem. Assoc.* 20, 373-8(1925)—A description accompanied by 9 photographs showing the kind of damage done to hides by the hair-follicle mite, *Demodex folliculorum*.

J. A. WILSON

Tanniferous galls of certain Bohemian trees. (Preliminary.) J. JEDLIČKA AND S. HULA. *J. Soc. Leather Trades Chem.* 9, 256-8(1925)—Galls produced by 20 kinds

of insects, from 8 species of trees, were examined 14 kinds contained tannin, pyro-catechol tannin being found in 13 cases H. B. MERRILL

The black wattle industry. T. R. SIM *Cuir tech* 14, 287-91(1925)—A review. H. B. MERRILL

Notes on the effect of hydrogen-ion concentration upon tannin analysis. J. S. ROGERS *J. Am. Leather Chem Assoc* 20, 370-3(1925); cf *C A* 19, 191.—Variations of less than 0.2 in  $pH$  value produced very small variations in values obtained for non-tannin J. A. WILSON

Determination of soluble matter in leather—committee report. T. J. MOSSER *J. Am. Leather Chem Assoc* 20, 378-82(1925)—With continued extn. of leather with water the ext. shows a higher proportion of tannin to nontannin with time. J. A. WILSON

Method for determining the acetyl number of tanning extracts and other materials and the use of the acetyl derivatives of tanning extracts for their separation and testing. R. LAUFFMANN *Leder tech Rundschau* 17, 49-51(1925)—To det. the Ac no., reflux 1.5 g. of liquid or 0.8 g. of the dry material and 10 cc. of  $Ac_2O$  for 20 min., then evap. the solvent and dry the residue to const. wt. Sulfite cellulose and syntans give sol., other exts. insol. Ac. derivs. The Ac nos. did not differ enough to be of use in identifying tanning materials. I. D. CLARK

Outline of a simple procedure for testing leather. ANON *Gerber* 51, 96-8(1925)—Tests, performable without app. or technical training, are described H. B. MERRILL

Biology of salt stains. H. PERICAUD *Cuir tech* 14, 280(1925), cf *C A* 19, 2423—Further discussion. H. B. MERRILL

Salt stains. ANR. *Cuir tech* 14, 272-3(1925); cf *C A* 19, 1961—A discussion H. B. MERRILL

Recent developments in the glue and gelatin industries. A. I. V. UNDERWOOD *Ind. Chemist* 1, 309-7(1925). E. H.

Transfer ink for marking leather (U. S. pat. 1,545,836) 26.

Borax and Boric Acid. In the Tannery and the Currying Shop. New York, Chicago and Oakland, Cal.: Pacific Coast Borax Co. Reviewed in *Chemicals* 24, 11 (1925).

Leather from shark skins, etc. A. EURENREICH and K. BENDIXEN *Brit* 228,310, Dec. 18, 1923. The dermal armor of shark skins or similar skins may be removed either before or after tanning. In the first case, the skin is treated with an aq. soln. of formic or other acid, milled or scrubbed and then tanned. In the second case the skin is tanned with vegetable or org. tanning substances and the dermal armor then removed after treatment with an aq. soln. of a "stronger" acid, e. g.,  $HCl$ .

## 30—RUBBER AND ALLIED SUBSTANCES

C. C. DAVIS

Effect of humidity in rubber testing. R. B. STRINGFIELD. *Ind. Eng. Chem.* 17, 833-5(1925).—The relative humidity to which rubber is exposed both before and after its vulcanization has a direct bearing on its phys. condition when cured, and only by maintaining this factor within fairly close limits (40-60%) can discordant results be avoided in the phys. testing of rubber. The influence varies with the compn. of the rubber mixt., becoming in general less marked in a given type of mixt. as the rubber content decreases. No generalizations can, however, be drawn concerning the influence of such agents as accelerators, for with a given type of mixt. the higher the humidity before curing the less stiff is the mixt. after curing with some accelerators and the stiffer it is after curing with others. All mixts., however, on exposure after curing stiffen as the humidity increases, the effect in this case being easily reversible. At a const. humidity an increase of temp. has the same effect as an increase of humidity at a const. temp. Judged by the const. value of the combined S in mixts. of differing phys. properties, the effect of humidity is purely phys. C. C. DAVIS

The ultra-violet microscope in the study of vulcanized latex globules. HENRY GREEN. *Ind. Eng. Chem.* 17, 802-3(1925)—The ultra-microscope is applied to the study of latex both before and after vulcanization with  $S_2Cl_2$ , and though no conclusion can be drawn in regard to the ultimate nature of vulcanization, certain visible effects

are plainly evident for the first time. Latex contains 3 types of globules which differ in shape and in size: 1) large pear-shaped globules, much smaller spherical globules and a third type of colloidal size. By compressing a film of latex so that the individual globules are visible, the no. of colloidal globules appear to increase enormously and the spheres of intermediate size appear in chain formation, perhaps because both these types have been squeezed from the interior of the large pear shaped parental globules. Treatment of *Ficus elastica* latex (cf Hauser, *C. A.* 19, 1962) with  $S_2Cl_2$ , in which the phenomena are particularly easy to observe, indicates that vulcanization takes place within the inner nucleus and not in the outer shell. On the other hand the *Hevea* globule, though the action is less discernible, appears to take up S uniformly. This is most evident in a dried film where the globules have become adherent, for on stretching there appear elastic connecting links which comprise the outer shell of the globules and which can be vulcanized. The S of  $CS_2$  does not absorb a wave length of  $0.275 \mu$ , but absorption occurs as soon as free S is in solution. C. C. DAVIS.

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Measuring effects of corona on rubber (HAUSHALTER) 4.

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**Vulcanizing rubber.** G. BRUNI U S 1,546,713, July 21. The reaction product of Br on thiocarbamide or other aromatic substituted thiourea is used as a vulcanization accelerator.

**Vulcanizing rubber.** M. L. WEISS U S 1,546,876, July 21. The reaction product of diphenylguanidine and dimethyldithiocarbamic acid is used as an accelerator, as may be also other compds. of the general formula  $R_2NCSSH \cdot HN \cdot C(NHR')_2$ , in which R and R' represent alkyl or aromatic groups and an aliphatic, alicyclic or aromatic group, resp. U S 1,546,877 specifies the use of a reaction product of guanidine and a mercapto benzo thiazole as an accelerator.

**Molding and vulcanizing rubber.** A. W. BRIGGS Brit. 228,241, Oct. 29, 1923. Crepe or similar rubber is combined with a layer of vulcanizable rubber compd. which preferably contains an accelerator, such as Zn diethyldithiocarbamate, to control shrinkage and enable vulcanization to be effected at a temp. which does not cause deterioration of the crepe.

**Spray desiccation and coating of rubber or other materials.** H. B. FABER U S 1,546,922, July 21. A liquid carrying a dissolved solid, e. g., a  $C_6H_6$  soln. of rubber, is sprayed into a hot gaseous desiccating medium and the suspended particles formed, immediately upon drying, are subjected to the action of a gaseous reacting medium, e. g.,  $SO_2$  or S chloride, which provides them with a coating.

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EDITED BY

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Chairman, Committee on the Chemistry of Colloids National Research Council

ASSISTED BY

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